THE CHEMISORPTION OF OXYGEN BY CHARCOAL

BY

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C O N T E N T S

	Page
Introduction	1
References (Introduction) ...	17
Experimental	
I Preparation and Characterisation of Charcoals ...	19
II Oxidation of Charcoal by Hydrogen Peroxide ...	35
III Action of Neutral Salt on L-Type Charcoal ...	55
IV Action of L-Type Charcoal on Sodium Arsenite ...	71
V Interaction Between Charcoal and Grignard Reagent ...	87
Discussion	107
References (Experimental and Discussion)	163
Summary	165.

INTRODUCTION.

Although it has long been known that oxygen is readily chemisorbed by charcoal, the nature of the oxygen layer has still to be elucidated. Of major importance in this connection are the phenomena observed when aqueous solutions of strong inorganic acids and bases are brought into contact with charcoal which has been activated by treatment with oxygen-containing gas at temperatures above about 250°. It is from this point of view that the problem of the oxygen layer has been approached in the present work.

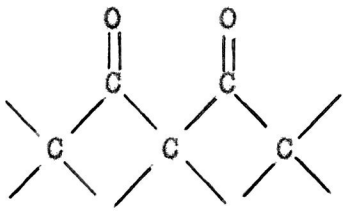
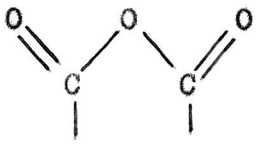
That the sorption of acids and bases is markedly affected in a definite and reversible manner by the temperature of activation was established mainly by the investigations of Kolthoff[1,2], Kruyt and de Kadt[3,4], Dubinin[5,6], and Schilov and co-workers[7,8], the results being published during the years 1927 to 1932. Prior to this period, it had become evident that charcoal could chemisorb oxygen, and some workers, notably Rhead and Wheeler[9], Langmuir[10], and Garner and co-workers[11,12,13], had already proposed formulations of the oxygen layer to account for the production of carbon dioxide and carbon monoxide by thermal decomposition of the layer. It was therefore natural to suppose that the sorption of acids and bases was closely associated with the chemisorption of oxygen, and attempts were

early made to interpret the sorption in terms of carbon "oxides" or carbon-oxygen "complexes" present on the surface of the charcoal, and decomposing, under suitable conditions, to give carbon dioxide or carbon monoxide.

The first systematic investigation of the influence of the temperature of activation was carried out by Schilov, Schatunovskaja and Tschmutov[7], who studied the sorption of sodium hydroxide and hydrochloric acid by sugar-charcoal which had been heated in air at temperatures between 250° and 1000°. It appeared that as the temperature was raised, the sorption of base passed through a maximum, while that of the acid exhibited a corresponding minimum. To account for their observations, Schilov[7,8,14] postulated the formation of two oxides on the surface of the charcoal, one (Oxide B) being capable of "adsorbing" acid, and the other (Oxide C) of "adsorbing" base. Oxide B was regarded as the primary product formed on the surface of the charcoal, and to be very stable, leaving the surface as carbon monoxide at the highest temperatures only. Oxide C was supposed to arise from oxidation of Oxide B, and to decompose readily into carbon dioxide and Oxide B, at temperatures lower than that at which Oxide B became unstable. From these assumptions it followed

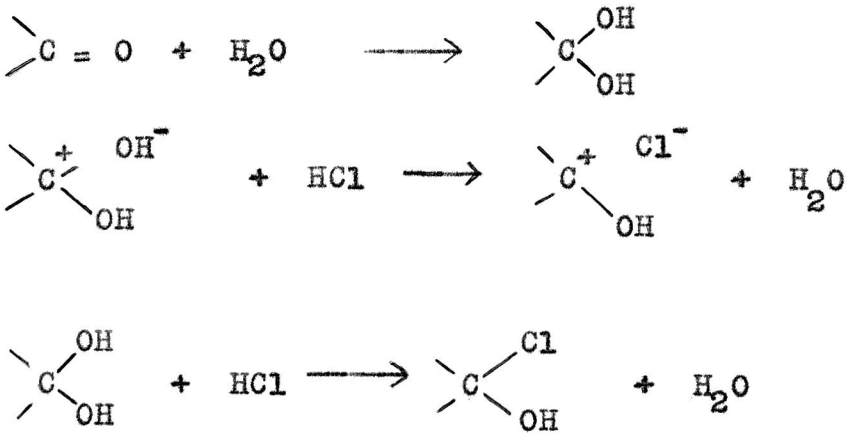
that the amount of Oxide C per unit mass of charcoal would pass through a maximum at a certain temperature of activation, the value of which would depend upon the manner in which the rates of formation and loss of Oxide C varied with the temperature. To avoid confusion, it should be added that Schilov postulated that a third oxide (A) existed, but under certain conditions other than those considered here.

Schilov provisionally pictured his oxides as follows:

B  C 

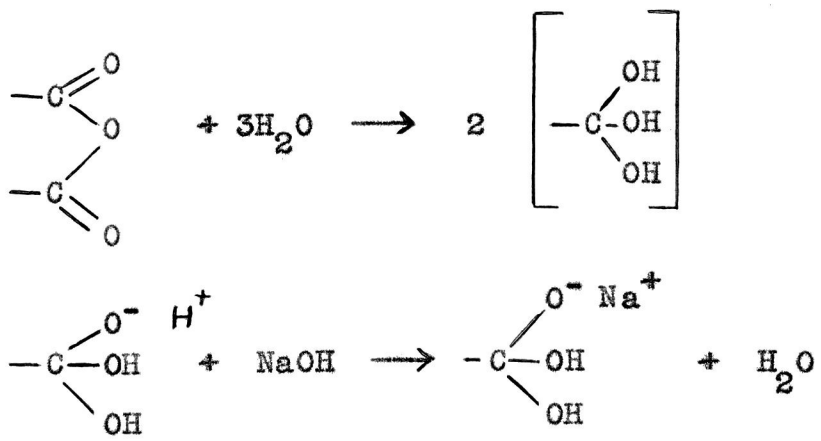
He supposed that they neutralised acids and bases respectively, according to the following schemes:

Oxide B



or

Oxide C.



Kruyt and de Kadt[4] suggested that the acidic nature of charcoal activated at 400° was due to the formation of carboxyl groups on the surface, the necessary hydrogen being furnished by the incompletely charred material which always appeared to be present in the interior of the charcoal particles. At 800° the carboxyl groups were not stable, decomposing to form carbon dioxide, but stable complexes of different nature, presumably carbonyl groups, were formed. It was thought that while acids might be neutralised by these, it was more probable that the uptake of acid was the result of physical adsorption of hydrogen ions on the bare carbon surface created by the decomposition of the carboxyl groups.

The existence of an acidic oxide was denied (in 1934) by Ockrent[15], who claimed to have proved that there was no chemisorbed oxygen present on the surface of charcoal which had been activated under

conditions favourable for the sorption of base. This claim was made because analysis of the charcoal appeared to show that all the oxygen present was in the form of water. Ockrent also observed that a large proportion of the water that was released on heating the charcoal in nitrogen, came off only at temperatures above the temperature of activation. He therefore concluded that the capacity for sorbing base was associated with the presence of a layer of strongly "adsorbed" water.

As part of an extensive investigation (1934-1938) of the influence of the temperature of activation on various properties of charcoal, King[16] re-examined the sorption of acids and bases. His results bore a general resemblance to those of Schilov and co-workers, but it was found that maximum sorption of base occurred with charcoal activated at about 400°, instead of 500° as reported by Schilov. King activated his charcoal with moist oxygen, but there is no reason to suppose that the use of this instead of air could account for the difference. Since King's charcoals were much more thoroughly activated than those of Schilov, he obtained at 400° material which sorbed large amounts of sodium hydroxide, but no hydrochloric acid. At about 800° the sorption of base fell to zero, while that of acid became very appreciable. At higher

temperatures sorption of base reappeared on a small scale, but this is not of special significance, since the charcoal was cooled in air and hence, as Steenberg[17] has shown, would be reactivated at 400° for a short period. Charcoals activated at 400° and 800° differed greatly in many respects. King attributed these differences to the existence of two "surface oxides", the one acidic and stable at low temperatures, the other basic and stable at high temperatures. While supporting Schilov's views in principle (as against Ockrent's theory), King made no mention of Schilov's specific proposals, and advanced none of his own.

Strickland-Constable[18] concluded from his own (very limited) data for a charcoal treated with nitrous oxide at 400°, that only a small portion of the chemisorbed oxygen was present as basic and acidic oxides. He advanced the view that the variation with temperature of the ratio of the amounts of carbon dioxide and monoxide produced by heating oxidised charcoal in vacuum, could be entirely explained by postulating the existence of a whole series of surface oxides having a wide range of decomposition temperatures. Ketonic and etheric linkages were quoted as examples of the types of linkage which might be expected to occur among these surface compounds.

In his very interesting monograph, published in 1944, Steenberg[17] has reviewed the whole subject of the sorption of electrolytes by charcoal, and has given an account of his own important investigations in this field. He introduces a convenient nomenclature to distinguish the two types of charcoal in question. The term "H-charcoal" is applied to charcoals which have been prepared by gas-activation at high temperatures (above about 750°) and which do not possess the power of sorbing strong bases. Charcoals which have been activated at lower temperatures and do sorb bases are called "L-charcoals". It was found by Steenberg that the L-character was most developed at 400°, thus confirming King's value. Steenberg's work was mainly confined to H-charcoals. He found it difficult to accept the existence of basic carbon oxides, since "substances of a corresponding nature and stability are not known in organic chemistry", and therefore he sought further information about the sorption of acids by charcoal.

Steenberg attaches great importance to experiments in which the influence of non-electrolytes upon the sorption of acids and bases was studied. He found that, if to a suspension of H-charcoal in hydrochloric acid, in which sorption equilibrium had been established, a soluble non-

electrolyte, e.g., antipyrene, acetone or ethyl alcohol, was added in sufficient quantity, almost quantitative desorption of the acid occurred. The same result was obtained if the suspension was shaken with an immiscible liquid in which the acid was insoluble, e.g., benzene, toluene or ethyl ether. However, no desorption of base from L-charcoal suspended in sodium hydroxide solution was observed under any of these conditions, although L-charcoals can sorb large amounts of non-electrolytes. Steenberg deduced from these results, that bases must be held by much stronger forces than those which cause sorption of acids. He concluded that it is reasonable to suppose that bases are bound chemically by acid carbon oxides which coat the surface of L-charcoals (at least partially), and that the uptake of acids by H-charcoals is due to physical (van der Vaals) adsorption of hydrogen ions on a bare carbon surface. Thus a view favoured by Kruyt and de Kadt (loc.cit.) was revived.

In a fairly recent paper, Wilson and Bolam[19] have described work designed to throw light on the mechanism of the sorption of bases by L-charcoal. Experiments similar to those of Ockrent were carried out with charcoal which had been well activated at 400° and which sorbed large amounts of base (ca. 315×10^{-5} equiv. NaOH per gm. charcoal). The

results obtained were quite different from those of Ockrent. Analysis of the charcoal revealed a much greater preponderance of oxygen over hydrogen, the ratio being about 30 to 1, instead of 8 to 1 as reported by him. Also, when the charcoal was heated in a stream of nitrogen, much less water was liberated than recorded by Ockrent, and the bulk of it came off well below 400°. These observations and other considerations led to the conclusion that Ockrent's theory was untenable. It was pointed out that the conditions of activation employed by him - treatment of a large mass of charcoal for a short time with air at 500° - would not be favourable for the production of material with a good content of oxygen. It may be added that experience gained in the present work indicates that with the apparatus used by Ockrent, much of the charcoal would not be brought into contact with the oxygen in the stream of activating air.

Wilson and Bolam found, in agreement with earlier workers, that when L-charcoal was heated in a stream of nitrogen, or in vacuum, at temperatures above 400°, the capacity for sorbing sodium hydroxide decreased, while that for sorbing hydrochloric acid increased. A systematic study was made of the decrease in base uptake, and of the amounts of carbon dioxide and monoxide evolved, as the result

of treatment at various temperatures and for various periods of time. The observations showed that the sorptive capacity did not disappear, until the charcoal was deprived of at least over 90 per cent. of its chemisorbed oxygen and possibly the whole of it. From the relationship between the decrease in sorption and the loss of oxygen, it appeared as though two carbon-oxygen complexes were present, the one (α) capable of sorbing base at the rate of 1 mole of NaOH to 2 atoms of oxygen, and the other (β) at the rate of 1 mole of NaOH to 4 atoms of oxygen.

The work of Wilson and Bolam showed that large amounts of oxygen can be chemisorbed at 400°, a content of 1 atom of oxygen to between 6 and 7 atoms of carbon being achieved in practice. This result does not support the opinion of Strickland-Constable (loc.cit.) that only a very few points on the carbon surface are available for the attachment of oxygen atoms to form surface oxides.

In all the investigations of the sorption of acids and bases so far mentioned (except that of Strickland-Constable) the charcoal was prepared from saccharose. Weller and Young[20] used zinc chloride-activated hard-wood charcoal for their work. However, their L-charcoals showed the same general behaviour as sugar charcoal. These workers were

the first to demonstrate that well-activated L-charcoals contain large amounts of chemisorbed oxygen. The ratio of oxygen to hydrogen in their most oxidised material was about 30 to 1, the figure obtained by Wilson and Bolam. Weller and Young also found that the heat of combustion of their L-charcoals varied linearly with the content of oxygen, and they concluded from this that the heat of chemisorption (deduced as 60,000-65,000 cal. per mole oxygen) was independent of the fraction of surface covered for the range of compositions studied, viz., 2.9 to 18.3 per cent. oxygen.

In the present research, attention has been directed mainly to certain aspects of the surface chemistry of L-charcoals, with the object of gaining information about the state of combination of the oxygen in the surface layer, particularly with respect to the sorption of bases, since there can be no doubt that the presence of chemisorbed oxygen is necessary for the uptake of base. Though the results of previous investigations cannot be said to exclude entirely the possibility that the base is physically adsorbed, there is the fact that carbon readily forms acidic compounds with oxygen, and account must be taken of the observations of Steenberg on L-charcoal. It therefore seemed reasonable to adopt, in the first place, the

conventional assumption that the base undergoes chemical reaction with acidic groups in the surface layer, of the type met with in organic chemistry. In consequence, the research is concerned, in part, with the detection and estimation of any such groups as may be present on the surface of the charcoal.

It was assumed that the hydrogen of acidic hydroxyl groups would exchange with the cations of simple neutral salts, as happens with phenolic and carboxyl exchange resins[21], and with colloidal stearic acid[22,23]. An attempt was therefore made to estimate such groups by treating the charcoal with aqueous potassium chloride and estimating the liberated acid. The exchange reactions may be represented by:

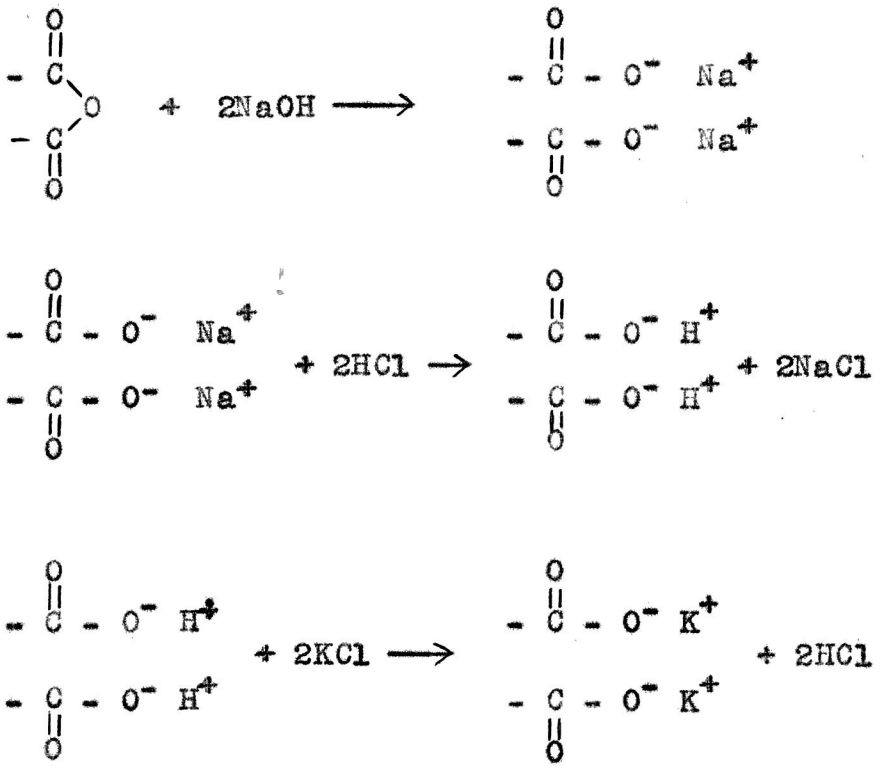
$$-\overset{|}{\underset{|}{C}}-O^- \; H^+ \; + \; KCl \longrightarrow -\overset{|}{\underset{|}{C}}-O^- \; K^+ \; + \; HCl$$

$$-\overset{O}{\overset{\|}{C}}-O^- \; H^+ \; + \; KCl \longrightarrow -\overset{O}{\overset{\|}{C}}-O^- \; K^+ \; + \; HCl$$

Kolthoff[2] and Chambers and King[24] observed that hydrogen ions were liberated from L-charcoals by the action of neutral salt, but their data are very restricted and the present work represents the first systematic investigation of the phenomenon (see Experimental, Section III).

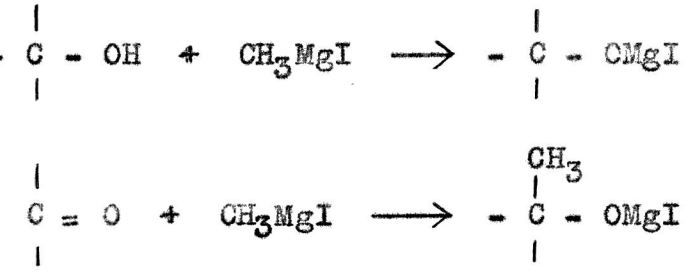
The ion exchange method was also applied to

the detection of acid anhydride groups. In these experiments (see Section III, Further Experiments), the charcoal was treated successively with sodium hydroxide and hydrochloric acid, and determination then made of the acid liberated by treatment with potassium chloride. It was supposed that the reactions could be represented by:



It will be seen that the formula proposed for the surface group is that advanced by Schilov[7,8] for his Oxide C. It is curious that although at one point he definitely describes the group as having the form of the anhydride of a carboxylic acid, he suggests an unorthodox scheme for the interaction with water.

In another part of the work, the interaction of L-charcoal (and H-charcoal, for purposes of comparison) with Grignard reagent was studied (see Section V). Villars[25] claims to have shown that hydroxyl and carbonyl groups were present on the surface of certain commercial carbons which contained relatively little oxygen. He assumes that hydroxyl and carbonyl groups on the carbon surface behave like similar groups in (small) organic molecules, and that they react with the Grignard reagent, methyl magnesium iodide, in the manner represented by the following scheme:



The gas liberated during the reaction is taken to be a measure of the hydroxyl oxygen, and any loss of Grignard reagent not accounted for in this way, is considered to be an estimate of the number of carbonyl groups present. Whatever may be the exact value of Villar's interpretation of his results, it is clear from his paper that interaction of some kind occurred, which was not observed if the carbon was freed from its oxygen by outgassing at a high temperature. Moreover, Villar's investigation is the only one of its kind recorded in the literature.

It was therefore considered of importance to study the behaviour of well-oxidised L-charcoal towards Grignard reagent, since this might reveal the presence of groups containing "active hydrogen", or the presence of carbonyl groups, or might throw light on some other features of the oxygen layer.

Since the experiments with Grignard reagent were carried out at a fairly high temperature (181°), it was necessary to consider the possibility that oxidation of the reagent by the chemisorbed oxygen might occur. An investigation was therefore made of the action of L-charcoal on aqueous solutions of sodium arsenite at room temperature, to ascertain whether oxidation by chemisorbed oxygen can occur (see Section IV). King[26] has examined the behaviour of charcoals towards arsenites and other easily oxidised substances, but, for reasons which will appear later (page 119), his results are inconclusive.

Schilov, Schatunovskaja and Tschmutov[7] mention that they examined the action of hydrogen peroxide solution on sugar charcoal, and found that treatment with 15 per cent. Perhydrol rendered the charcoal capable of sorbing base. No detailed information is given. Later, King[26] studied the influence of sugar charcoal on the rate of decomposition of hydrogen peroxide solution. From his

results it appeared that using charcoal which had been activated in oxygen at 920° (H-charcoal), the rate of evolution of oxygen was high at first, but decreased after a relatively short time to a low constant rate. King concluded that the H-charcoal had been oxidised to L-charcoal.

In view of the foregoing, it appeared worthwhile to ascertain if treatment with hydrogen peroxide at ordinary temperatures would provide a more convenient method of preparing well-oxidised charcoal of high base-sorbing capacity, than treatment with oxygen at about 400°. An examination was therefore made, at the commencement of the research, of the interaction of charcoal with hydrogen peroxide. It was found that departure from the conventional method of preparing L-charcoal was not justified, but the investigation provided interesting information in connection with the chemisorption of oxygen.

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E X P E R I M E N T A L.

I. PREPARATION AND CHARACTERISATION OF CHARCOALS.

In the present work three types of charcoal have been used. They may be conveniently designated "unactivated", "L-type", and "H-type", the last two in keeping with Steenberg's terminology (see page 7). Their characteristics were as follows (cf. Wilson and Bolam[1]).

Unactivated charcoal. Material which had been purified by heating in vacuum at 825-850° for about six hours, and which received no further treatment. This charcoal had a relatively small specific surface area, and sorbed only very small amounts of base.

L-type charcoal. This was prepared from unactivated charcoal by heating in a stream of oxygen at about 400° for an appropriate time. Since the material was activated and oxidised, it possessed a much higher specific surface area than the unactivated charcoal, and the sorption of base was markedly enhanced.

H-type charcoal. This was prepared from L-type material by heating in vacuum at 825-850° for about six hours. The product, being activated, had a specific surface not less, and probably greater, than that of L-type charcoal. On the other hand, as the result of loss of oxygen, the capacity for sorbing base was very small.

Preparation of Crude Charcoal.

The charcoal was prepared from ANALAR sucrose by heating small batches of the latter in pyrex glass basins (9 cm. diameter) with bunsen burners. The basin was half-filled with sucrose, placed on wire gauze, and a large clock-glass clamped above to act as a protection against the entrance of atmospheric dust. When the sugar had been converted into a thick black tar, it was ignited and allowed to burn out. At this stage the product was heated with a full bunsen flame, to expel volatile matter. The first lot of charcoal from each basin was rejected, and thereafter, only the easily detachable flaky portions were collected. This material was crushed in a large porcelain basin with a nickel spatula, transferred to silica basins, covered with pyrex clock-glasses and heated with the full flame of a Méker burner for forty minutes. To ensure uniform treatment, the charcoal was stirred every five minutes. Finally the charcoal was ground in an agate mortar and stored in a well-stoppered bottle. An ash determination, carried out by heating 1 gm. portions in porcelain basins, gave 0.06% of residue.

Figs. 1 and 2.

Fig.1.

A. Furnace
S. Furnace tube
B. Pyrex cones
C. Cold wrappings
T. Pyrex taps
D. Grease trap
E. Cold trap
M. McLeod gauge
P. Speedivac pump
R. Thermocouple
L. Silica bath.

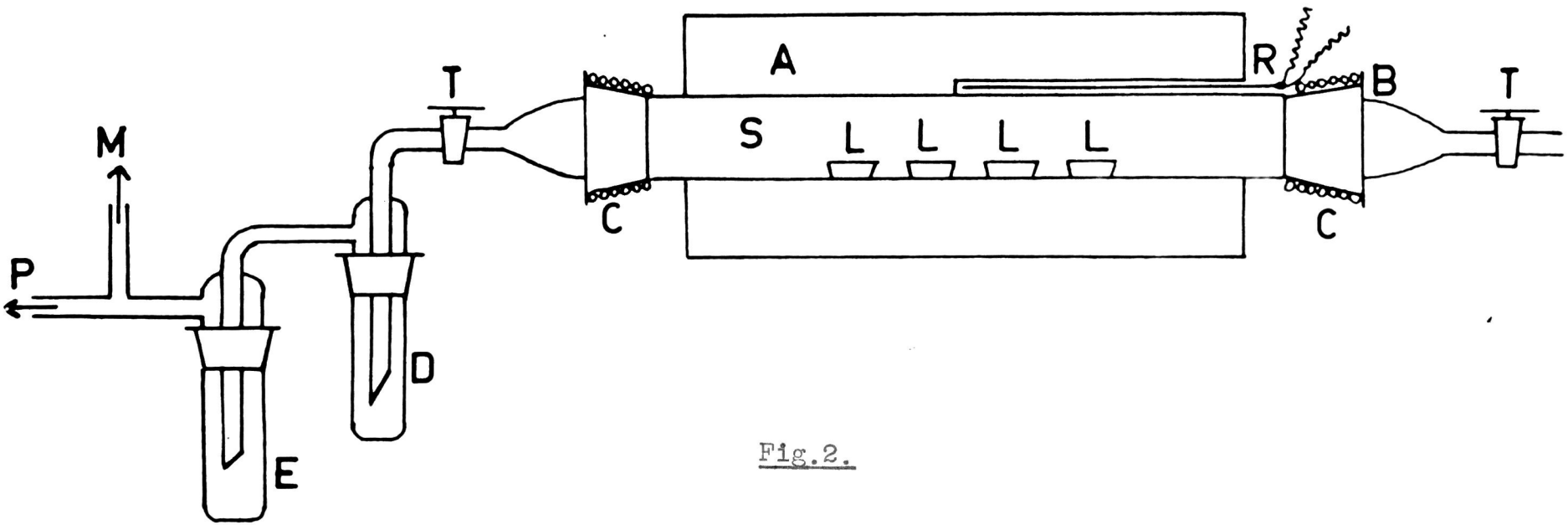
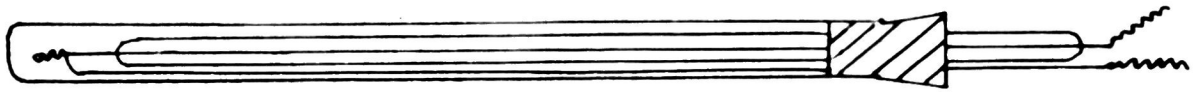


Fig.2.



Preparation of Unactivated Charcoal.

Purification of the crude charcoal was effected by heating under vacuum in the apparatus illustrated in Fig.1 (page 21). The transparent silica furnace tube (length 3'3"; external bore 32 mm.) terminated in sockets which were fitted with B.40 pyrex cones for connection to the remainder of the apparatus. The ground-ends of the furnace tube were lubricated with "Silicone" high vacuum grease, and kept cool by cloth wrappings saturated with water flowing from a constant-head device. All other joints and stopcocks were lubricated with Edwards "Apiezon L" grease.

The Gallenkamp electric furnace could be maintained at any desired temperature over the range 350° to 1000°, by a calibrated "Sunvic" control unit. In an actual experiment the furnace was heated at full current (i.e., regulator setting at maximum) until the chosen temperature was reached, and then by suitable adjustment of the regulator this temperature could be maintained. A thermocouple made of two nichrome wires (Ferry and Bright Ray) was used to measure temperatures, and was calibrated against a Cambridge platinum/platinum-rhodium thermometer. The construction of the thermocouple is shown in Fig.2 (page 21), and the e.m.f. produced was measured by means of a Cambridge valve electrometer. The plot of e.m.f. against temperature gave

a very good straight line, and temperatures could be read to at least $\pm 5^{\circ}$.

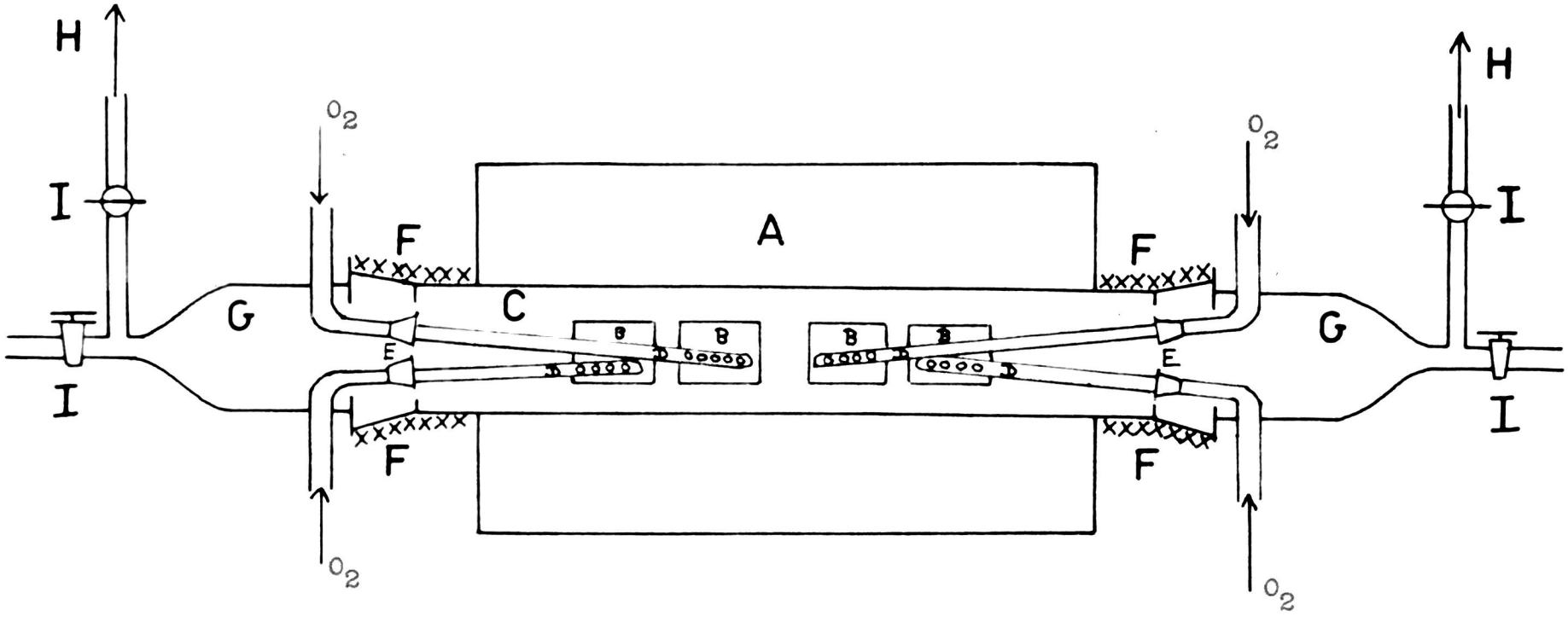
The purification of the charcoal was carried out as follows. Silica boats filled with charcoal were pushed into the centre of the furnace tube, and the assembly of the apparatus completed. The furnace tube was evacuated, the temperature then raised (in approximately 45 minutes) to 825° or 850°, and the charcoal heated under these circumstances for approximately six hours. At the end of this period the current was switched off and the charcoal allowed to cool overnight, in vacuum in the furnace tube. While the furnace was heating up, an appreciable amount of water vapour was evolved from the charcoal and condensed at the cold ends of the furnace tube. At the same time some fine charcoal was ejected from the silica boats and carried down the vacuum line, being caught in the grease trap D, and thus prevented from contaminating the pump oil.

After treatment, the charcoal was removed from the furnace tube, a long pyrex rod, bent at one end to form a small hook, being used to withdraw the boats. The material from the various boats was thoroughly mixed and stored in a clean dry bottle fitted with a rubber stopper.

In all, seven batches of unactivated charcoal were used during the work. They are differentiated as U_1, U_2 ..... U_7.

Fig.3.

Fig.3.



A. Furnace
B. Silica boats
C. Silica tube
D. Distributers
E. B.10 pyrex sockets
F. Cold wrappings
G. B.40 cones
H. Oxygen outlet to flometer
I. Pyrex taps.

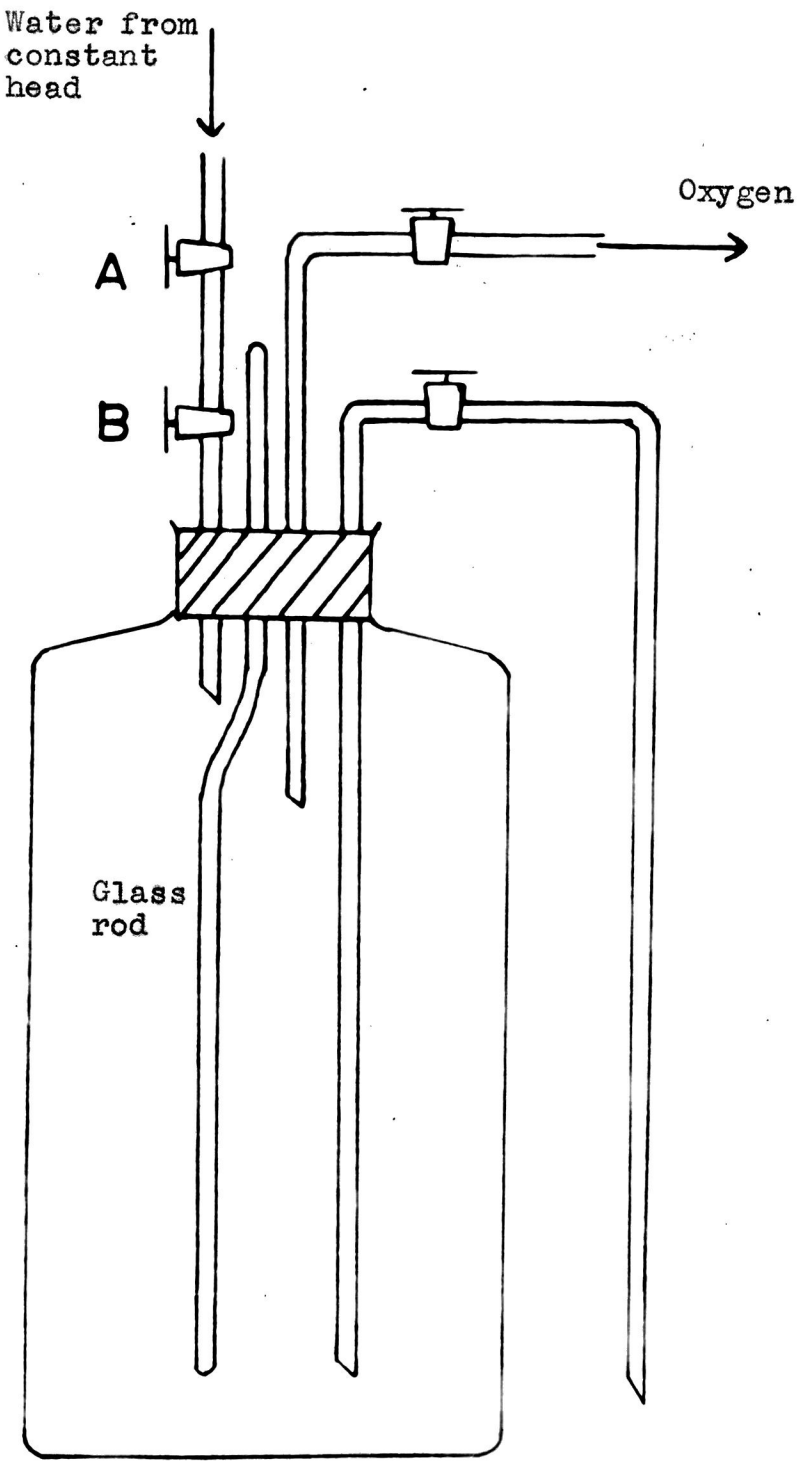
Preparation of L-Type Charcoal.

Wilson and Bolam[1] prepared this charcoal by heating 12 gm. of unactivated charcoal contained in two silica boats at about 400° in a stream of oxygen for 24 hours. The oxygen was passed over the heated charcoal at 5 ml. per minute for 12 hours in each direction. After this treatment the charcoal could sorb about 310 x 10^{-5} equivalents of sodium hydroxide per gm. and the overall loss of charcoal incurred was greater than 50%. It was thought possible to improve the efficiency of the oxidation process by (a) decreasing the depth of charcoal in the boats and (b) introducing the oxygen gas at the surface of the charcoal.

The apparatus designed to effect the improvement is shown in Fig.3 (page 24). From the plan it can be seen that oxygen was passed into the furnace tube via four side arms, and flowed along pyrex glass tubes to supply each boat independently. The arrangement was such that the charcoal in each boat received approximately the same amount of oxygen. For proper distribution of the gas, the end of each tube was pierced with a line of small holes whose diameters were so graded that there was no serious drop in gas pressure between the first and the last. The distributers were fixed a few millimetres above the charcoal surface, and could be disconnected from

Fig.4.

Fig.4.



the apparatus at the ground-glass joints E, when the furnace tube was to be used for high temperature work (825° or 850°).

Oxygen was fed into the apparatus in the following manner. The 20-litre bottle shown in Fig.4 (page 26) was completely filled with water and the water then expelled by introducing the gas under pressure from a cylinder until the bottle was filled. A steady flow of gas into the apparatus was obtained by running water into the bottle from a constant-head device. The taps A and B served to regulate the rate of inflow of water. With tap A fully open, tap B could be adjusted to give the required rate of passage of gas, as measured by the flowmeter attached at the exit end of the apparatus. Thereafter tap B remained untouched, tap A being used to stop the inflow of water when required. The oxygen was dried by bubbling it through two concentrated sulphuric acid bottles.

The results of the experiments performed in order to find a satisfactory oxidation procedure are collected in Tables 1-3 (pages 28 - 30). In Experiments 1, 2 and 3 the temperature of activation, rate of gas flow and weight of charcoal were kept constant, but the time of oxidation was varied. It will be seen that using a time period of activation of six hours, at a temperature of 400° and a gas

Table 1.

Influence of Oxidation Procedure on Loss of Charcoal.

Exp. No.	Average wt. of charcoal per boat (gm.)	Time	Rate	Temp. of oxidns. (°C)	Wt. of charcoal before oxidation (gm.)				Wt. of charcoal after oxidation (gm.)				% loss in weight				Average loss in wt. (%)
					Boat 1	Boat 2	Boat 3	Boat 4	Boat 1	Boat 2	Boat 3	Boat 4	Boat 1	Boat 2	Boat 3	Boat 4	
1	4.01	4	5	400	4.01	3.99	4.02	3.99	3.35	3.35	3.41	3.31	16.52	16.11	15.22	17.10	16.24
2	3.98	6	5	400	4.01	4.01	3.90	3.98	3.25	3.41	3.10	3.18	19.00	15.00	20.47	20.10	18.64
3	3.98	14	5	400	-	-	-	-	-	-	-	-	-	-	-	-	58.00
4	4.09	14	2	400	4.07	3.98	3.93	4.37	2.89	3.30	3.47	3.32	29.00	17.00	12.00	24.00	21.00
5	3.92	4	5	500	-	-	-	-	-	-	-	-	-	-	-	-	18.00
6	3.91	6	5	400	3.95	3.83	3.97	3.89	3.28	3.14	3.09	3.31	17.20	18.00	22.00	15.20	18.10
7	6.05	6	5	400	5.92	6.13	6.01	6.12	5.33	5.68	5.58	5.52	10.14	7.30	7.18	9.80	8.60
8	5.03	6	5	400	5.00	5.08	5.02	5.01	4.29	4.32	4.28	4.04	14.23	15.11	14.66	19.29	15.82

Time = time of oxidation, in hours.

Rate = rate of oxygen flow per distributer, in c.c. per minute.

Table 2.

Influence of Oxidation Procedure on Sorption of Base.

Exp. No.	Weight of charcoal shaken with 25 ml. 0.2N NaOH (gm.)				Change in titre on 10 ml. 0.2N NaOH (ml. 0.1N HCl)				Equivalents NaOH sorbed per gm. charcoal ($\times 10^5$)				Equivalents NaOH sorbed by 1gm. charcoal after mixing ($\times 10^5$)
	Boat 1	Boat 2	Boat 3	Boat 4	Boat 1	Boat 2	Boat 3	Boat 4	Boat 1	Boat 2	Boat 3	Boat 4	
1	.3012	.2984	.2977	.2968	1.92	1.82	1.68	2.03	159.2	152.5	144.3	171.0	155.0
	.3068	.3042	.3008	.3020	2.02	1.90	1.76	2.00	163.0	156.2	146.3	165.0	
2	.3040	.3014	.3020	.3012	2.35	1.94	2.45	2.58	195.2	160.9	202.9	220.6	208.0
	.3082	.2985	.3015	.3022	2.41	1.90	2.61	2.64	195.5	159.1	216.4	218.4	
3	-	-	-	-	-	-	-	-	-	-	-	-	268.0
4	-	-	-	-	-	-	-	-	-	-	-	-	155.0
5	-	-	-	-	-	-	-	-	-	-	-	-	87.0

? 187.

Table 3.

Influence of Oxidation Procedure on Sorption of Base.

Expt. No.	Wt. of charcoal shaken with 25 ml. 0.2N NaOH (gm.)							
	Boat 1		Boat 2		Boat 3		Boat 4	
	T	B	T	B	T	B	T	B
6	.3032	.3050	.3052	.3082	.3026	.3010	.3095	.3081
7	.3011	.3040	.3026	.3041	.3019	.3018	.2987	.3020
8	.3140	.3000	.3080	.2984	.3120	.3052	.3020	.3128

Expt. No.	Change in titre on 10 ml. 0.2N NaOH (ml. 0.1N HCl)							
	Boat 1		Boat 2		Boat 3		Boat 4	
	T	B	T	B	T	B	T	B
6	2.68	2.74	2.47	2.54	2.60	2.62	2.69	2.62
7	2.50	2.01	2.14	1.61	2.23	1.68	2.52	2.12
8	2.78	2.59	2.62	2.57	2.69	2.61	2.72	2.78

Expt. No.	Equivalents NaOH sorbed by 1 gm. charcoal ($\times 10^5$)g							
	Boat 1		Boat 2		Boat 3		Boat 4	
	T	B	T	B	T	B	T	B
6	220.7	224.9	202.2	206.2	214.9	217.6	199.5	212.4
7	207.1	165.4	176.8	132.8	184.6	139.1	211.0	175.6
8	221.3	215.0	212.6	215.3	215.5	213.7	225.2	222.1

T = top layer of charcoal in boat.

B = bottom layer of charcoal in boat.

flow rate of 5 ml. per distributer per minute, when the weight of charcoal was 4 gm. per boat, a satisfactory oxidised product was obtained and a considerable reduction in loss of charcoal effected (Experiment 2). On increasing the period of activation from six to fourteen hours (Experiment 3), the percentage loss of charcoal rose from ca. 19% to 58%, but the base sorption only increased by 60×10^{-5} equivalents per gm. of charcoal. Alternatively, if the period of activation was less than six hours, the base sorption of the product became too low, viz. 155×10^{-5} equivalents per gm. (Experiment 1). In Experiment 4, the conditions of Experiment 3 were reproduced except that the gas flow rate was changed from 5 ml. to 2 ml. Again, the loss of charcoal was low (21%) but the base sorption fell from 268×10^{-5} to 155×10^{-5} equivalents per gm. Experiment 5 resembles Experiment 2 but the temperature of activation was 500° instead of 400°. This resulted in a product showing very poor base sorption.

In Experiments 6, 7 and 8 the quantity of charcoal was varied to ascertain the optimum weight necessary for the production of uniform material. In these experiments, the top and bottom of each charge of charcoal were carefully sampled, and the base sorptions determined. From the data in

Tables 1 and 3 (pages 28 and 30), it is evident that when the weight of charcoal per boat was 4 to 5 gm., uniform oxidation took place, but a 6 gm. charge gave a material in which the bottom layers were poorly oxidised. These results indicated that the optimum weight of charcoal per boat was 5 gm. The dimensions of the rectangular boats were 5.6 cm. x 2.5 cm. x 1.0 cm. A 5 gm. portion of charcoal filled a boat to a depth of 0.7 cm.

With one exception (see page 154), L-type charcoal was prepared according to the conditions which obtained in Experiment 8. It was found in practice that the base-sorption of material prepared in this way was always within a few per cent of 222×10^{-5} equivalents per gm. charcoal, the value obtained in the above experiment. This charcoal was adequate for the purpose and could be obtained in a much shorter time, and with much less loss, than the charcoal of higher sorbing capacity used by Wilson and Bolam[1]. It would appear from the present work (Experiment 3) that to obtain the latter material, lengthy treatment (ca. 24 hours) and high loss of charcoal are unavoidable.

Preparation of H-Type Charcoal.

This material was prepared from L-type charcoal, by heating the latter in vacuum at a temperature of about 825-850° for 6 hours in the apparatus

shown in Fig.1 (page 21). In this case, the silica boats were completely filled with charcoal and the experimental procedure adopted was the same as that described for the purification of crude charcoal on page 23.

Measurement of Sorption of Base.

Small quantities of charcoal were accurately weighed into pyrex tubes of about 75 ml. capacity, fitted with ground-glass stoppers. 25 Ml. of alkali of approximately 0.2N concentration was introduced into each tube, the stopper inserted and coated with paraffin wax, which served to seal the tube perfectly and hold the stopper in position during shaking. The charcoal was shaken with the solutions for 24 hours, by fixing the tubes radially to a slowly rotating circular wooden disc. Each sorption determination was duplicated. Between experiments the tubes were washed free from paraffin wax with hot water, rinsed with distilled water, and dried in an electric oven.

After shaking, each tube was allowed to stand until most of the charcoal had settled out. The wax was then scraped off and the solution decanted into a pyrex tube and centrifuged. The supernatant liquid was decanted into a pyrex test-tube and 10 ml. portions measured out with a pipette and titrated with approximately 0.1N hydrochloric acid. As it

was just possible to take two 10 ml. portions for titration in each case, the titrations were duplicated. Preliminary trials without charcoal showed that no "blank" correction was necessary. Hence the sorption was obtained from the difference between the titre obtained after contact with the charcoal, and that obtained by titration of 10 ml. of the untreated solution of base.

II. OXIDATION OF CHARCOAL BY HYDROGEN PEROXIDE.

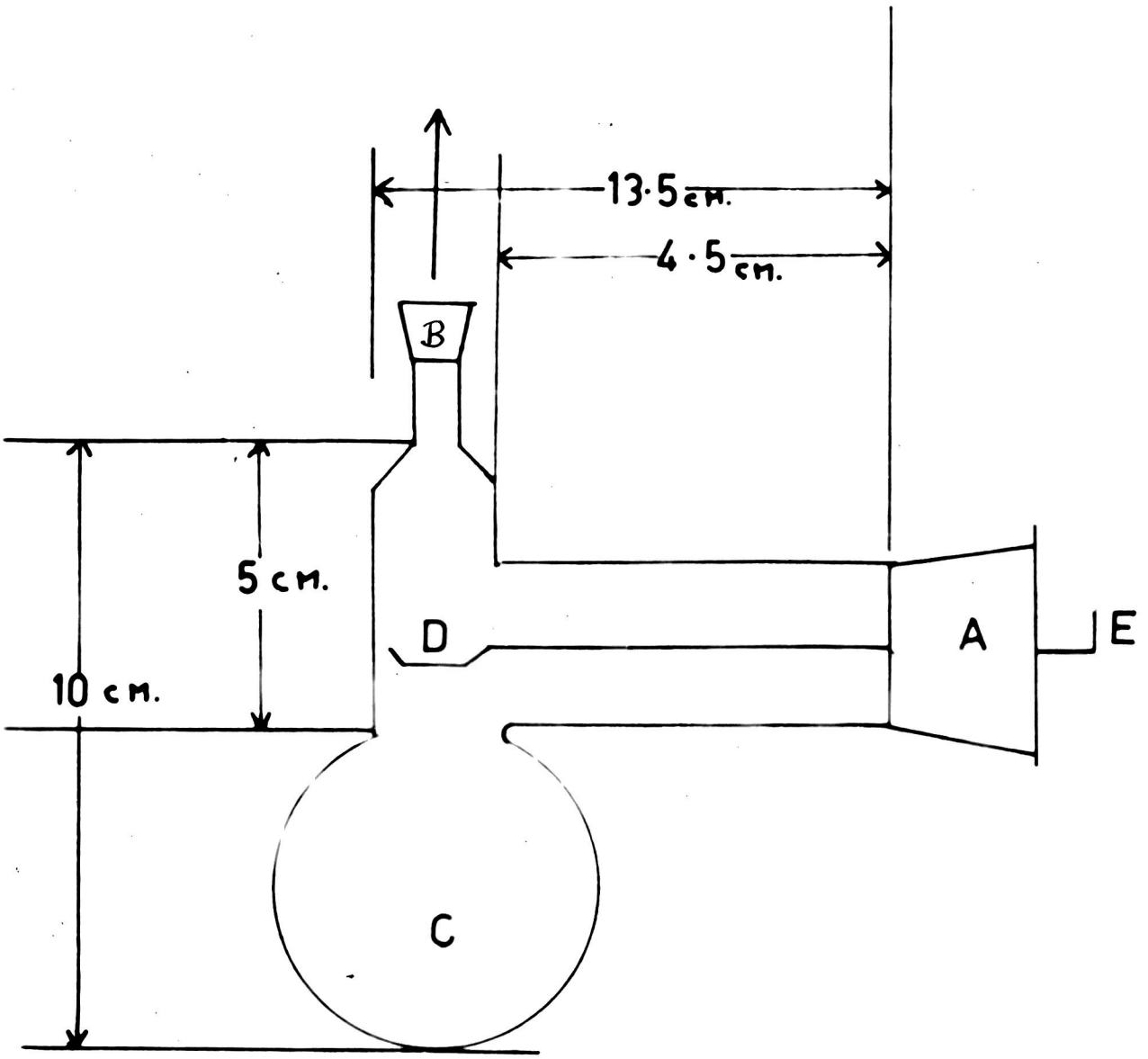
Measurement of Rate of Decomposition.

The rate of decomposition of hydrogen peroxide by charcoal was determined by shaking the charcoal in suspension in hydrogen peroxide solution at a definite rate, and measuring the gas evolved by means of a burette system. Essential features of the apparatus employed are shown in Figs.5,6 and 7 (pages 36,37, 39). The hydrogen peroxide solution was placed in a pyrex glass reaction vessel (capacity 230 ml.), which was fixed rigidly to a shaker and connected by means of a flexible rubber coupling to a glass capillary tube which led to a gas burette.

The rate of decomposition of hydrogen peroxide in solution depends, among other factors, on the rate of agitation (cf. Fowler and Walton[2]). It has been shown that increase in agitation beyond a certain value has no effect upon the reaction rate. In preliminary experiments with the apparatus described, no increase in the rate of gas evolution was observed when the agitation rate was increased from 400 to 450 shakes per minute. Therefore a value of 400 shakes per minute was chosen for the subsequent experiments.

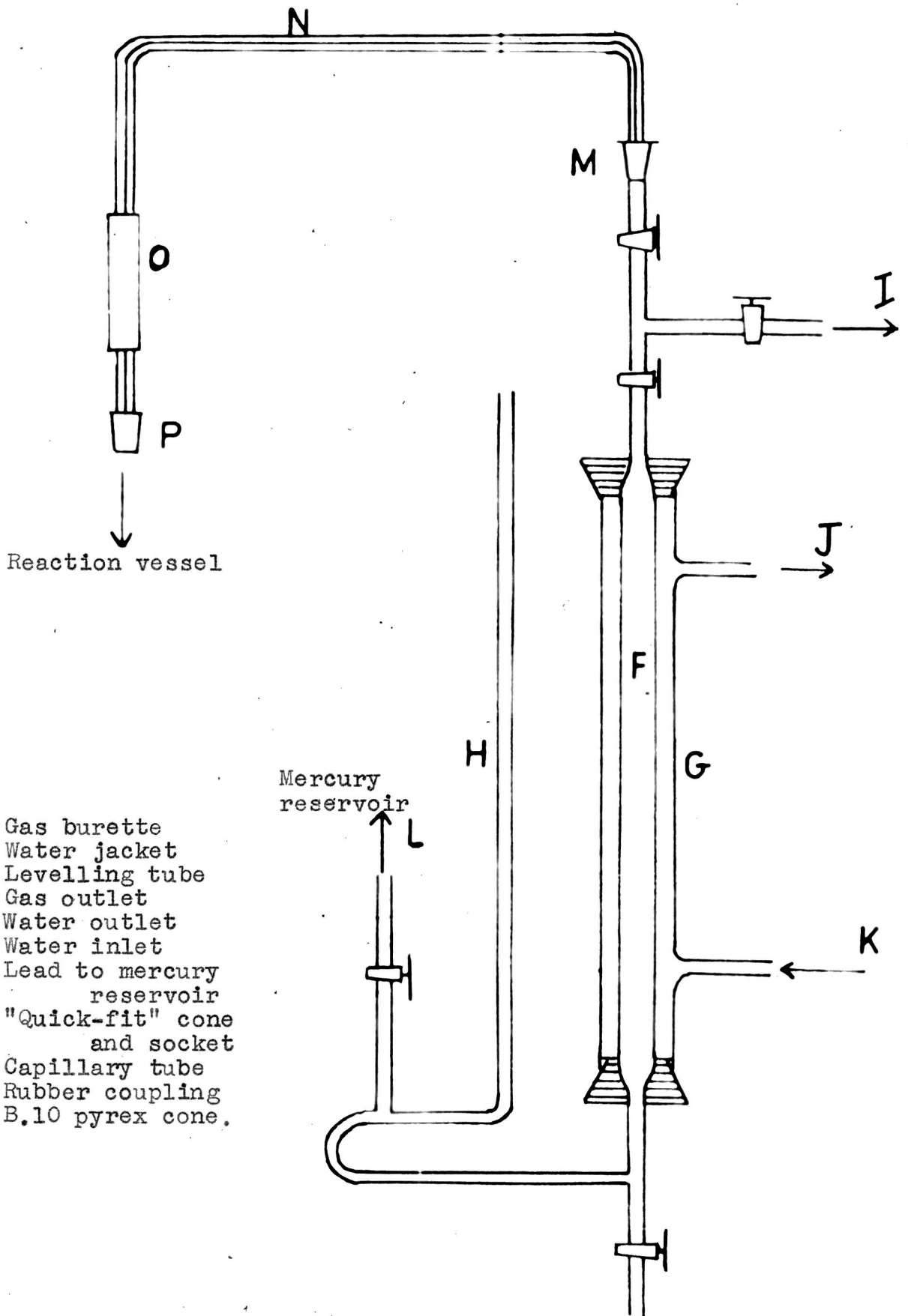
The reaction vessel (Fig.5) was so designed that the charcoal and hydrogen peroxide solution could be brought together under the same thermostat

Fig.5.



A. B.40 pyrex cone and socket
B. B.10 pyrex socket
C. Reaction vessel
D. Spoon
E. Pyrex handle.

Fig.6.



F. Gas burette
G. Water jacket
H. Levelling tube
I. Gas outlet
J. Water outlet
K. Water inlet
L. Lead to mercury reservoir
M. "Quick-fit" cone and socket
N. Capillary tube
O. Rubber coupling
P. B.10 pyrex cone.

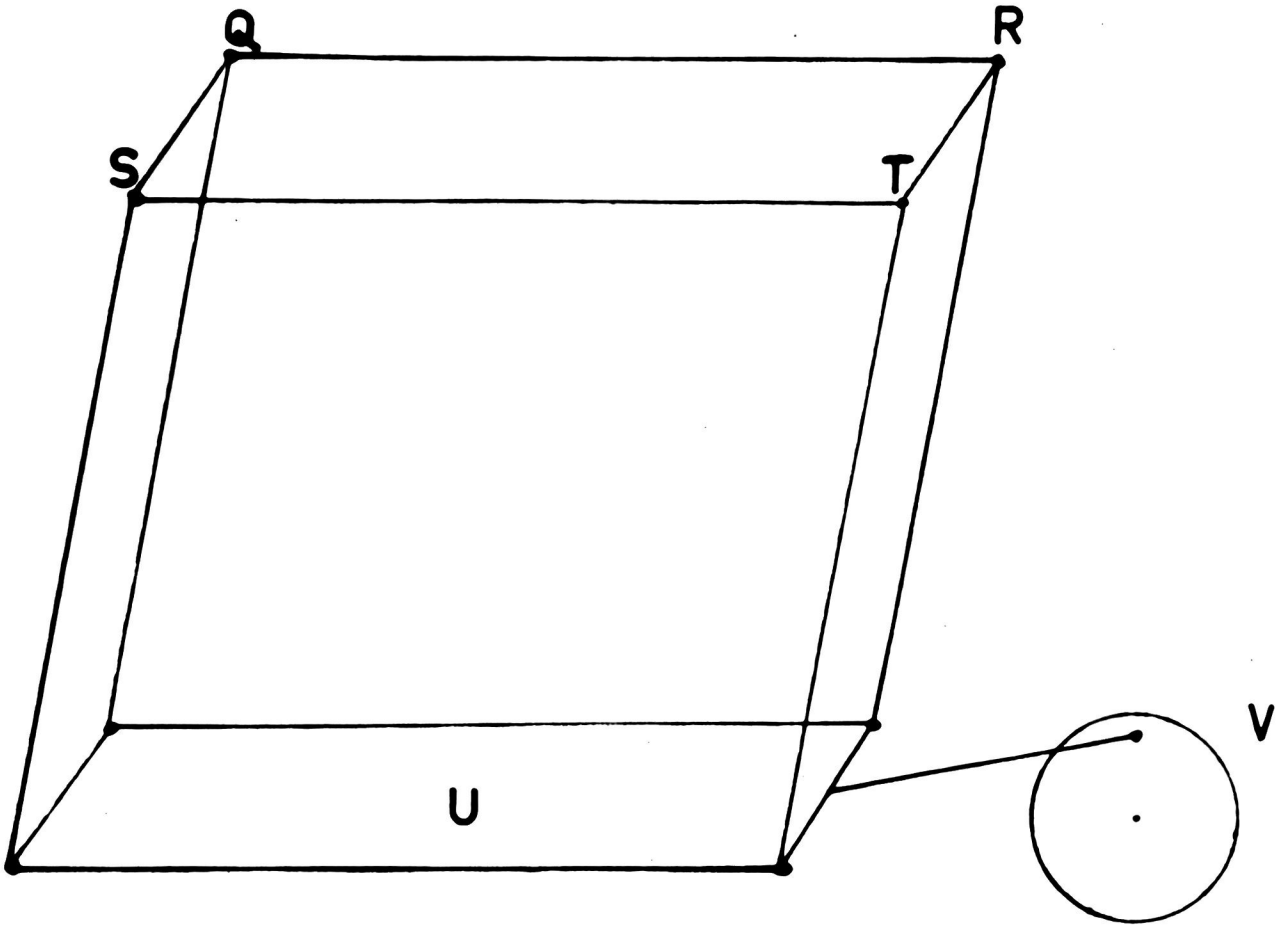
conditions. During an experiment, the reaction vessel C was immersed to the top of B in a water bath maintained at $20^{\circ} \pm 0.01^{\circ}$ by means of a regulator of the usual mercury-toluene type with a "Sunvic" relay. The water in the bath was kept in motion by an electrically-driven stirrer.

The gas burette (Fig.6) was enclosed in a glass jacket G through which water was circulated, the temperature of the water being ascertained from a thermometer placed in a U-tube connected to the outlet J. Mercury was used as the liquid in the gas burette and the pressure in the gas space (as indicated by the mercury levels in F and the narrow open glass tube H) could be adjusted by raising or lowering a mercury reservoir attached by pressure tubing to L. The burette was connected to the reaction vessel by means of cone P which fitted the socket B of flask C (Fig.5).

The shaker (constructed of "mild" steel) consisted of a cradle U (Fig.7), freely suspended at the points Q, R, S and T from a rigid system of girders, and given a reciprocating motion by means of an eccentric V, driven by an electric motor. An adjustable resistance was connected in series with the motor so that the rate of shaking could be maintained at any chosen value.

In each experiment, 25 ml. of hydrogen peroxide solution of known concentration was

Fig.7.



Q, R, S, T. Suspension points
U. Cradle
V. Eccentric.

measured accurately (by means of a calibrated pipette) into the reaction vessel, and approximately 1 gm. of charcoal was weighed accurately into the spoon D. The ground-glass surfaces of the vessel were greased with "Silicone" high vacuum grease, and the spoon D placed in position. The vessel was then firmly attached to the cradle, and connected to the gas burette. After some thirty minutes had been allowed to elapse for the establishment of thermal equilibrium, the spoon was turned through 180° (by means of the handle E), thus bringing the charcoal into contact with the hydrogen peroxide solution, and shaking commenced. At suitable time intervals the mercury was brought to the same levels in F and H (Fig.6), and the reading in F recorded. The values of the barometric pressure, and the temperatures of the gas burette and of the water in the thermostat tank were also recorded.

Determination of Degree of Oxidation of Charcoal.

The extent of base sorption of a hydrogen peroxide treated charcoal was used as a measure of its degree of oxidation. At the end of an experiment, the charcoal was collected on a sintered-glass filter and washed with distilled water until the filtrate was shown to be free from hydrogen peroxide. The material was then air-dried, and the base sorption determined as described on page 33.

The reagent used to detect hydrogen peroxide in the washings was prepared by adding 2 ml. of 7N ammonia mixed, with two drops of 6% $K_3Fe(CN)_6$, to 5-6 drops of silver nitrate solution. This gave a precipitate of white rhomboid prismatic crystals of $Ag_4Fe(CN)_6$ in the presence of hydrogen peroxide. An appreciable turbidity is produced with 12 drops of the reagent in 20 ml. of solution containing 0.1 mg. of hydrogen peroxide per litre.

Estimation of Hydrogen Peroxide.

Titration with deci-normal potassium permanganate was employed in the estimation of the hydrogen peroxide content of the solutions, the potassium permanganate being standardised with ferrous ammonium sulphate according to the method described by Cumming and Kay[3]. All hydrogen peroxide solutions were reduced to a strength of approximately 10 volumes and their concentrations determined in the following manner.

10 Ml. of the solution was diluted to 250 ml. with distilled water in a standard flask. After mixing, 25 ml. of this solution was diluted to about 300 ml. with distilled water in a conical flask, 25 ml. of dilute sulphuric acid added, and the contents of the flask titrated with standardised potassium permanganate solution. The concentrations of the hydrogen peroxide solutions are ex-

pressed as c.c. of oxygen per ml. of solution.

Sources of Hydrogen Peroxide.

Material from three sources, as under, was employed.

Laporte-Commercial. This was the 10 volume solution commonly supplied by Laporte Chemicals Ltd.

Laporte-Pure-Distilled. By the courtesy of Laporte Chemicals Ltd., a quantity of their "pure" product, stated to be free from inhibitor, was obtained. Before use, this material was distilled.

Specially Prepared. Material prepared by the author, as described below.

Preparation of Hydrogen Peroxide.

It was decided to employ the following method, evolved by MacKenzie and Ritchie[4], since this had proved successful for the rapid preparation of small quantities of concentrated pure hydrogen peroxide solution. This method is based on that described by Kilpatrick, Reiff and Rice[5].

Preparation of a Crude Solution of Hydrogen Peroxide.

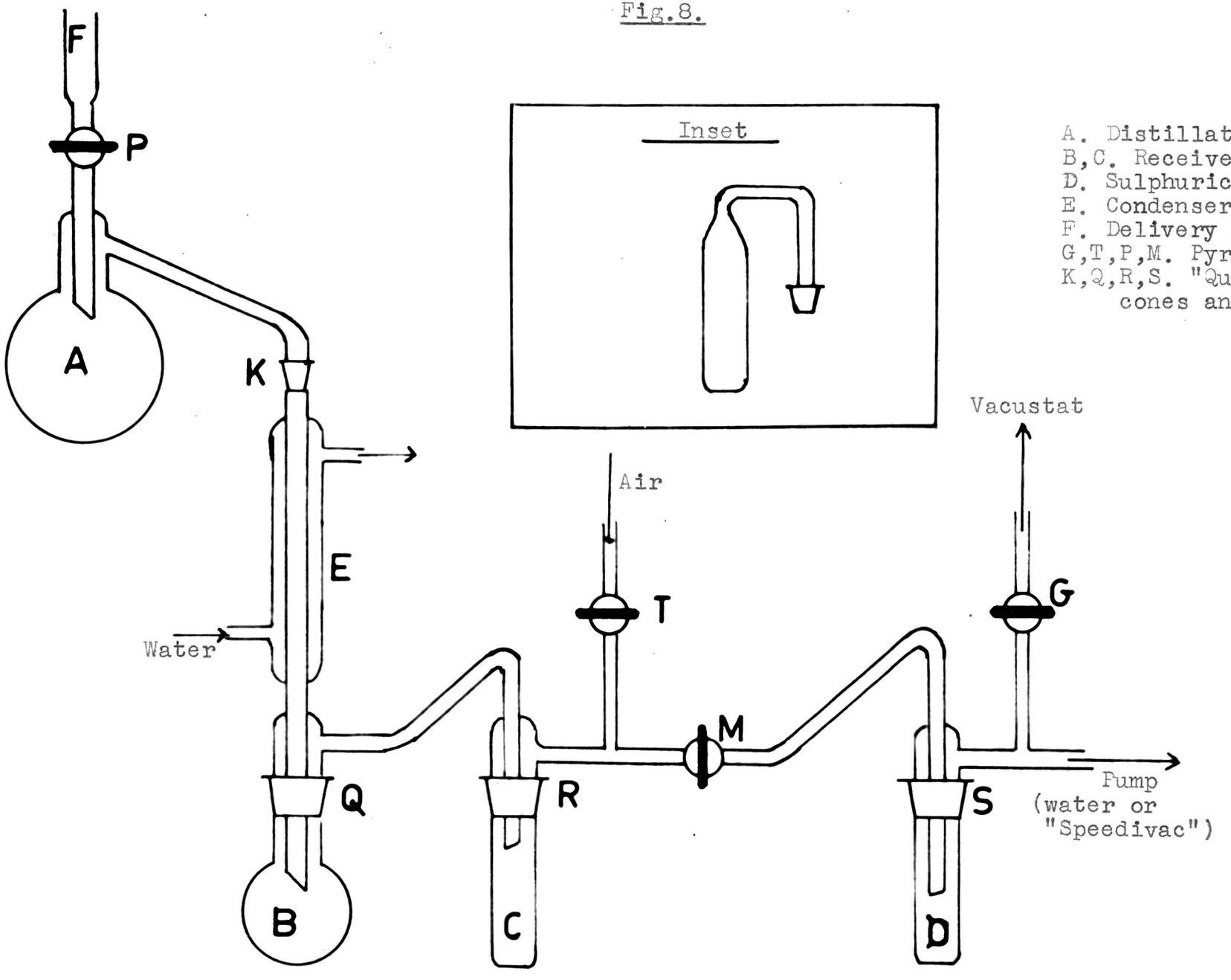
A crude solution of hydrogen peroxide was prepared from sodium peroxide and 20% sulphuric acid, both reagents being of ANALAR quality. The sodium peroxide was added in small quantities, with constant stirring, to 100 ml. of the acid (prepared by diluting concentrated acid with distilled water) in

a pyrex beaker placed in a freezing mixture, until an amount equivalent to 95% of the acid had been introduced. During this time the temperature of the mixture was kept below 10°. If the temperature was allowed to rise above this, considerable decomposition of the hydrogen peroxide occurred. After standing for about one hour at 0°-5°, the crystals of sodium sulphate decahydrate which had separated were filtered off. Since it has been reported[5] that these crystals can retain up to 20% of the peroxide formed, they were washed several times with ice-cold water, the amount being carefully chosen so that, while the greater part of the peroxide was removed from the crystals, the solution was not excessively diluted. It was found that the optimum amount of washing water was approximately 200 ml. for the crystals obtained from 100 ml. of sulphuric acid. The final solution contained about 6% of hydrogen peroxide.

Concentration and Purification of Hydrogen Peroxide.

The crude solution still contained sodium sulphate, and removal of this, together with further concentration of the solution, were carried out simultaneously by vacuum distillation. Fig.8 (page 44) shows the specially constructed distillation apparatus, which consisted entirely of pyrex glass (since hydrogen peroxide attacks rubber).

Fig.8.



A. Distillation flask
B,C. Receivers
D. Sulphuric acid trap
E. Condenser
F. Delivery funnel
G,T,P,M. Pyrex taps
K,Q,R,S. "Quick-fit" cones and sockets.

Experimental Procedure. The distillation flask A (250 ml.), condenser E, and receivers (B = 250 ml., C = 10 ml.) were washed with distilled water, assembled in position and dried by evacuation with the oil-pump. Air was then admitted through T as far as tap M, and the flask A charged with approximately 100 ml. of crude hydrogen peroxide solution through F. Receiver B was cooled in ice-water, and C immersed in a freezing mixture of ice and salt (temperature about -15°). The pressure was now reduced to 12-15 mm. by means of a water-pump, and flask A was heated gradually in a water-bath to about 25°, where the first signs of distillation appeared. The temperature was then increased very slowly to 35° and the bulk of the distillation carried out at this point. Whenever the volume of solution in A fell to 50 ml., the vacuum in the flask was broken and a fresh charge of crude solution introduced through F, to bring the total volume in A back to 100 ml.

The bulk of the first 200-250 ml. of liquid collected in receiver B consisted mainly of water and was discarded. When all the crude solution had been added, the temperature was kept at about 35° until all but 20-30 ml. of solution had distilled. At this point receiver B was quickly replaced by a tube of 15 ml. capacity, and the apparatus evacuated

by an oil-pump. As the volume of solution remaining in A decreased, some crystals separated, and the temperature of the water-bath was raised to maintain a reasonable rate of distillation. When the crystals in the flask appeared dry, the tube at B (containing the first fraction of value) was replaced by a duplicate tube, and the second fraction of distillate obtained by raising the temperature to 100°. This second fraction, containing about 70% hydrogen peroxide, was mixed with the first fraction, yielding about 15 ml. of 30% peroxide.

In all, 30 ml. of solution were prepared from two batches of crude solution. To effect further concentration and to remove any trace of chloride, the solution was redistilled after the addition of a few crystals of silver sulphate[5]. Since the volume of solution was small, flask A was replaced by the specially constructed tube shown in Fig.8 (inset). The distillation was carried out exactly as before, except that receiver B (15 ml. capacity) was cooled by an ice-salt freezing mixture (-15°), and C by a carbon dioxide - acetone mixture (-80°). Only the last two fractions from the redistillation contained an appreciable concentration of peroxide, and on mixing yielded about 10 ml. of 75% solution. This material was diluted with distilled water to give the required concentration.

Precautions. (1). The purpose of employing the two receivers B and C, in the manner described, was to assist in concentrating the peroxide in B by the distillation of (mainly) water from B to C.
(2). The condenser E was placed in a vertical position, since when it was inclined at the usual angle, the most highly concentrated fraction of the distillate tended to adhere as droplets to the wall. The solution could be removed only by passing hot water through the condenser, resulting in appreciable decomposition of the peroxide.
(3). A water-pump was used for evacuation in the earlier stages of the distillation, to avoid, as far as possible, the very inconvenient bumping and frothing of the solution which occurred when the oil-pump was employed.
(4). The concentrated sulphuric acid trap D prevented thickening of the pump-oil (as observed by Maas and Hatcher[6], and Kilpatrick, Reiff and Rice[5]) by any vapours escaping condensation in the receivers. Since during distillation the temperature of the trap tended to rise, it was kept immersed in ice-cold water. It was found necessary to change the sulphuric acid several times during a distillation, since its volume increased by absorption of water and the entry-tube became blocked.

(5). It was found essential to raise the temperature of the peroxide solution very slowly during distillation if bumping and frothing were to be kept to a minimum, and undue decomposition of peroxide avoided.

(6). All ground-glass surfaces of the apparatus were lubricated with "Apiezon L" grease, except joint K which became hot during distillation and for which "Picein" wax was therefore used.

(7). Changing of receivers was carried out very quickly to avoid loss of peroxide.

Results.

The results of the experiments carried out to examine the action of hydrogen peroxide solution on charcoal are collected together in Tables 4 - 7 (pages 49-54). In the eighteen runs carried out, the type of charcoal, the source and concentration of hydrogen peroxide, and the time of reaction were varied, while the reaction temperature was kept constant at 20°. For purposes of comparison, the values shown for the volume of gas evolved, and the amounts of base sorbed after treatment, are derived from the observed data, and refer in all cases to one gm. of charcoal. The results are discussed on page 147.

Table 4.

Charcoals.

Run	Type of Charcoal	Batch	Remarks
1	Unactivated	U_1	Heated in vacuum at 850° for 6 hours
2	"	U_2	"
3	"	U_3	"
4	"	U_4	Heated in vacuum at 825° for 6 hours
5	"	U_4	"
6	"	U_5	Heated in vacuum at 850° for 6 hours
7	"	U_5	"
8	"	U_5	"
9	"	U_5	"

Table 4 (continued).

Charcoals.

Run	Type of Charcoal	Batch	Remarks
10	L-type	L_1	Unactivated charcoal (U_4) oxidised by method of Wilson and Bolam[1].
11	Unactivated	U_4	Heated in vacuum at 825° for 6 hours.
12	-	-	-
13	-	-	-
14	H-type	H_1	Unactivated charcoal (U_5) heated in O_2 at 400° for 6 hours, then heated in vacuum for 6 hours at 825°.
15	"	H_1	"
16	"	H_2	Unactivated charcoal (U_5) heated in O_2 at 400° for 6 hours, then heated in vacuum for 6 hours at 850°.
17	"	H_3	Unactivated charcoal (U_6) heated in O_2 at 400° for 6 hours, then heated in vacuum for 6 hours at 850°.
18	"	H_3	"

Table 5.

Hydrogen Peroxide Solutions.

Run	Material	Titre (ml. 0.1N $KMnO_4$) per 25 ml. solution	Concentration (C.C.O_2 per ml. solution)
1	Laporte-Commercial	44.70	10.0
2	"	44.70	10.0
3	"	44.70	10.0
4	"	31.45	7.0
5	"	36.22	8.1
6	Laporte-Pure-Distilled	45.30	10.2
7	"	44.60	10.0
8	"	49.90	11.2
9	"	43.50	9.7
10	Specially Prepared	49.20	11.0
11	"	49.20	11.0
12	"	49.20	11.0
13	"	49.20	11.0
14	Laporte-Pure-Distilled	80.10	17.9
15	"	80.10	17.9
16	"	434.00	97.2
17	Specially Prepared	78.20	17.5
18	"	78.20	17.5

Table 6.

Gas Evolution from Hydrogen Peroxide-Charcoal Reaction.

Time (min.)	Volume of oxygen evolved per gm.charcoal at N.T.P. (Runs 1-9)								
	1	2	3	4	5	6	7	8	9
30	-	29.6	29.9	28.8	28.9	35.5	35.2	33.3	34.5
32	33.4	-	-	-	-	-	-	-	-
60	-	47.2	47.3	43.1	44.2	51.6	50.2	47.1	49.1
62	48.7	-	-	-	-	-	-	-	-
90	-	60.1	59.5	55.4	55.9	64.1	62.1	58.6	-
120	-	68.9	71.3	62.3	66.2	73.5	71.7	68.4	69.9
122	72.6	-	-	-	-	-	-	-	-
150	-	78.1	-	75.5	-	82.6	80.2	76.7	78.3
152	81.9	-	-	-	-	-	-	-	-
179	89.3	-	-	-	-	-	-	-	-
180	-	86.4	87.8	83.4	-	-	-	84.1	86.1
210	-	94.4	95.3	-	89.9	-	-	90.5	92.8
240	-	101.0	102.2	-	96.3	-	101.6	97.0	98.8
270	-	107.1	108.9	-	-	109.9	-	-	104.5
285	-	-	-	-	105.3	-	-	105.4	106.8
300	-	113.1	114.4	110.5	-	115.3	113.0	107.7	109.5
315	-	-	-	113.2	-	-	-	-	-
330	-	-	119.6	-	112.8	-	-	-	-
360	-	-	124.6	121.4	117.7	-	-	-	-
365	-	123.7	-	-	-	-	-	-	-
390	-	-	129.0	126.6	121.9	-	-	-	-
450	-	-	136.6	134.9	-	-	-	-	-
510	-	-	143.6	-	-	-	-	-	-
600	-	-	153.1	153.3	147.1	-	-	-	-
630	-	-	155.7	-	150.1	-	-	-	-
725	-	164.4	-	-	-	-	-	-	-
810	-	-	168.7	179.2	165.1	-	-	-	-
900	-	169.2	174.4	185.5	171.3	-	-	-	-

Table 6 (continued).

Gas Evolution from Hydrogen Peroxide-Charcoal Reaction.

Time (min.)	Volume of oxygen evolved per gm. charcoal at N.T.P. (Runs 10-18)								
	10	11	12	13	14	15	16	17	18
30	6.4	41.7	0.6		68.8	69.1	165.3	-	-
32	-	-	-		-	-	-	29.7	54.3
60	7.9	49.0	0.8		-	-	-	41.3	76.3
62	-	-	-		-	-	237.9	-	-
90	-	49.2	0.9		120.9	118.7	-	-	-
120	11.2	49.7	1.1		139.2	137.2	329.0	61.4	109.6
122	-	-	-		-	-	-	-	-
150	12.8	50.2	1.4		152.9	152.2	364.0	-	-
152	-	-	-		-	-	-	-	-
179	-	-	-		-	-	-	-	-
180	14.2	50.7	1.5		166.5	165.5	395.0	77.6	133.4
210	15.5	50.9	1.6		-	177.6	-	-	-
240	16.7	51.3	1.7		188.3	188.7	-	-	-
270	-	51.6	1.9		-	198.9	-	-	-
285	-	51.9	-		-	-	-	-	-
300	-	-	2.1		207.2	208.0	-	-	-
315	-	-	-		-	-	-	-	-
330	21.2	-	-		-	-	-	-	-
360	-	-	-		-	-	-	-	-
365	-	-	-		-	-	-	-	-
390	23.2	-	-		-	-	-	-	-
450	25.2	-	-		-	-	-	-	-
510	-	-	-		-	-	-	-	-
600	-	-	-		-	-	-	-	-
630	-	-	-		-	-	-	-	-
725	-	-	-		-	-	-	-	-
810	-	-	-		-	-	-	-	-
900	-	-	-		-	-	-	-	-

Volume of O_2 after 24 hours = 1.2 ml.

Table 7.

Effect of Treatment with Hydrogen Peroxide on Sorption of Base.

Charcoal	Period of Treatment (min.)	Run	Hydrogen Peroxide		Increase in sorption of base by 1 gm. of charcoal (10^{-5} equiv.) $\triangle$ NaOH
			Source	Concn. (c.c. O_2 per ml.)	
U_1	179	1	Laporte-Commercial	10.0	6.0
U_5	300	9	Laporte-Pure-Distilled	9.7	9.4
U_5	300	7	"	10.0	10.5
U_5	300	6	"	10.2	10.0
U_4	285	11	Specially Prepared	11.0	8.8
U_5	300	8	Laporte-Pure-Distilled	11.2	9.2
U_4	900	4	Laporte-Commercial	7.0	20.1
U_4	900	5	"	8.1	19.7
U_2	895	2	"	10.0	20.6
U_3	900	3	"	10.0	20.2
H_3	180	17	Specially Prepared	17.5	46.8
H_3	180	18	"	17.5	56.3
H_2	180	16	Laporte-Pure-Distilled	97.2	56.3
H_1	300	14	"	17.9	44.7
H_1	300	15	"	17.9	48.6
H_1	24 hours	-	"	97.2	72.2

III. ACTION OF NEUTRAL SALT ON L-TYPE CHARCOAL.

Measurement of Amount of Liberated Acid.

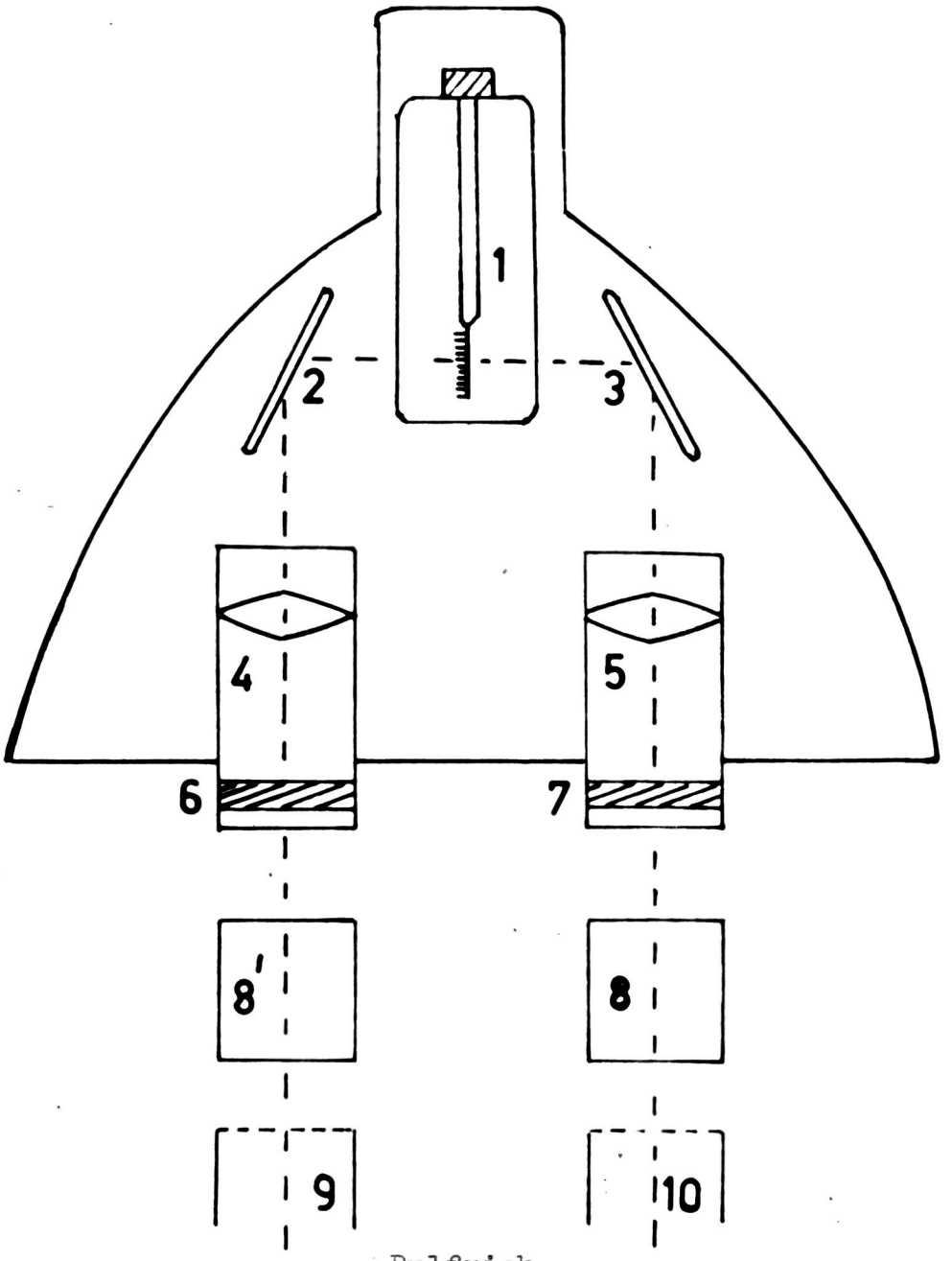
A colorimetric method was employed, using Congo-red as the indicator, to measure the concentration of the liberated acid.

The colorimeter (by Carl Zeiss) is shown in plan in Fig.9 (page 56). Light from an 8 volt 30 watt lamp (1) is directed by two mirrors (2) and (3) into the condenser lenses (4) and (5). Ground-glass screens (6) and (7) are placed in the paths of the light beams to decrease the intensity of illumination.

In the present work 10 ml. of the "test" solution was placed in the rectangular cell (8), and the same volume of distilled water (comparison liquid) in the similar cell (8^1). 20 Drops, of constant volume, of Congo-red (B.D.H. Standard Stain : 0.1% aqueous solution) were added to each cell, and the intensities of the transmitted beams compared by means of a Pulfrich photometer (by Carl Zeiss).

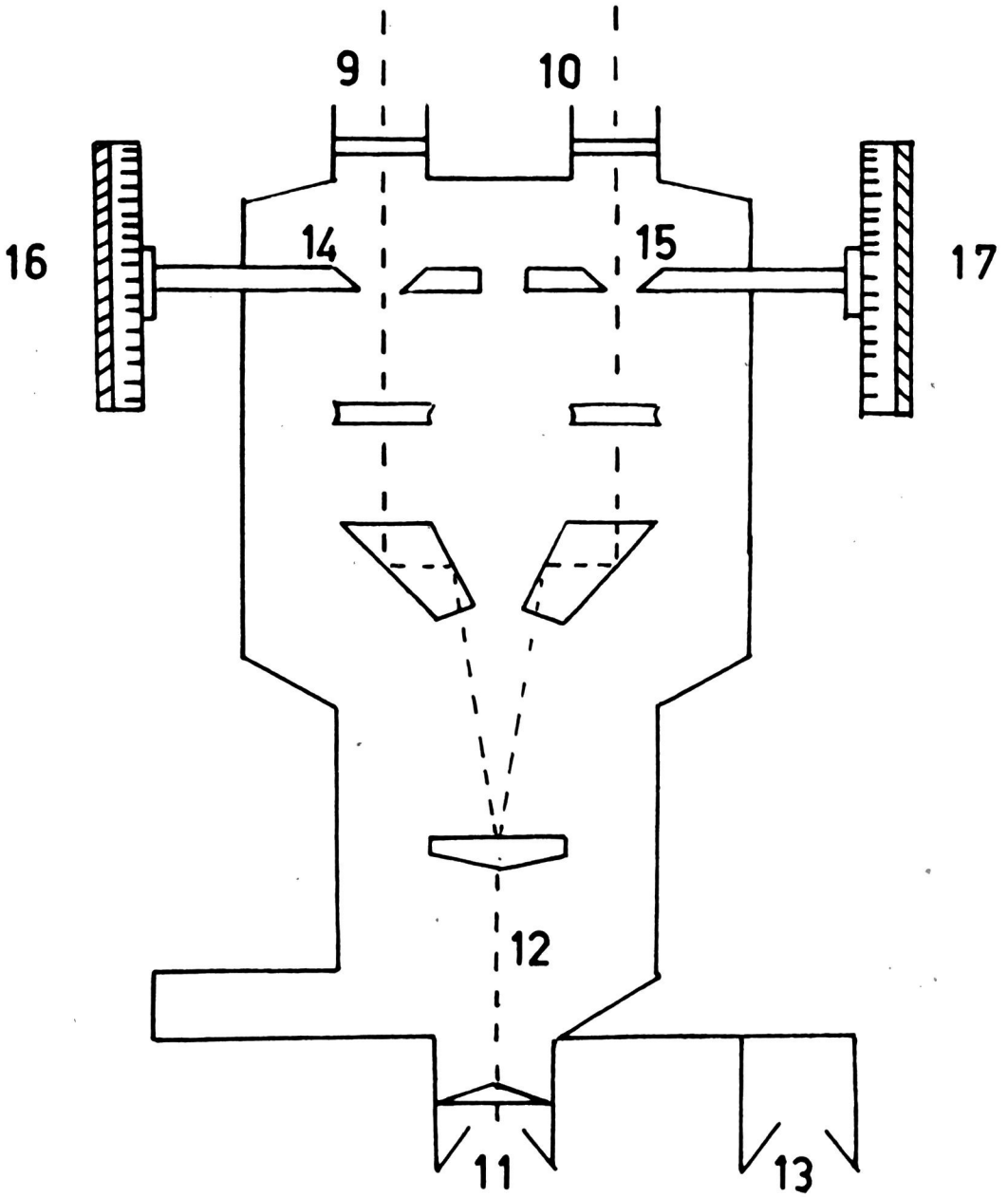
The principle of the photometer is shown in plan in Fig.10 (page 57). Both beams of light, the "test" beam through (10) and the comparison beam through (9), are brought into the circular field of the eyepiece at (11) by a system of lens

Fig.9.



Pulfrich photometer here.

Fig.10.



and prisms. The left-hand and right-hand halves of the eyepiece field are illuminated by the "test" and comparison beams respectively, since the optical arrangement reverses the positions of the beams. A suitably coloured glass filter may be placed in the path of the beams at (12), and a blind eyepiece (13) is provided to cover the unused eye.

The brilliancies of the two halves of the field can be adjusted by varying the sizes of the square apertures (14) and (15) by means of micrometer screws controlled by the drum-heads (16) and (17). Each drum-head is engraved with a scale so arranged that the reading is zero when the aperture is fully closed, and 100 when fully open.

For the purposes of the present work, the right-hand drum of the photometer (i.e., the drum controlling the size of the aperture through which passes the light emerging from the cell containing the "test" liquid) was set at position "74" on the scale, and was never moved from this setting. The left-hand drum was now adjusted until equal brightness was obtained in the two halves of the field of vision, and the drum-setting was then read. The orange filter N°. S.61 (supplied by Zeiss) was found to be satisfactory for use with the Congo-red solutions.

The method was calibrated, and the reproduci-

bility of results checked by measurements on solutions of hydrochloric acid, with and without potassium chloride.

The calibration data are recorded in Table 8 (page 60) and graphed in Fig.11 (page 61). The systems examined were as follows.

A. Solutions containing hydrochloric acid alone. In each case x ml. of 0.0001025N HCl were diluted to 100 ml. with water, x being given the values 10, 20, 30, 40 and 50.

B. Solutions containing hydrochloric acid + 0.1N KCl. In each case x ml. of 0.0001025N HCl were diluted to 100 ml. with (50 - x) ml. of water and 50 ml. of 0.2N KCl. The values of x were as above.

C. Solutions containing hydrochloric acid + 0.02N KCl. In each case x ml. of 0.0001025N HCl were diluted to 100 ml. with (50 - x) ml. of water and 50 ml. of 0.04N KCl. The values of x were as above.

Thus the concentrations of the acid (see left-hand column of Table 8) were the same for all three series, 0.1N KCl being present in all the experiments under B, and 0.02N KCl in all those under C.

The 0.0001025N HCl was prepared from a stock 0.1N solution of the acid, by suitable dilution. In each series the duplicate determinations of the

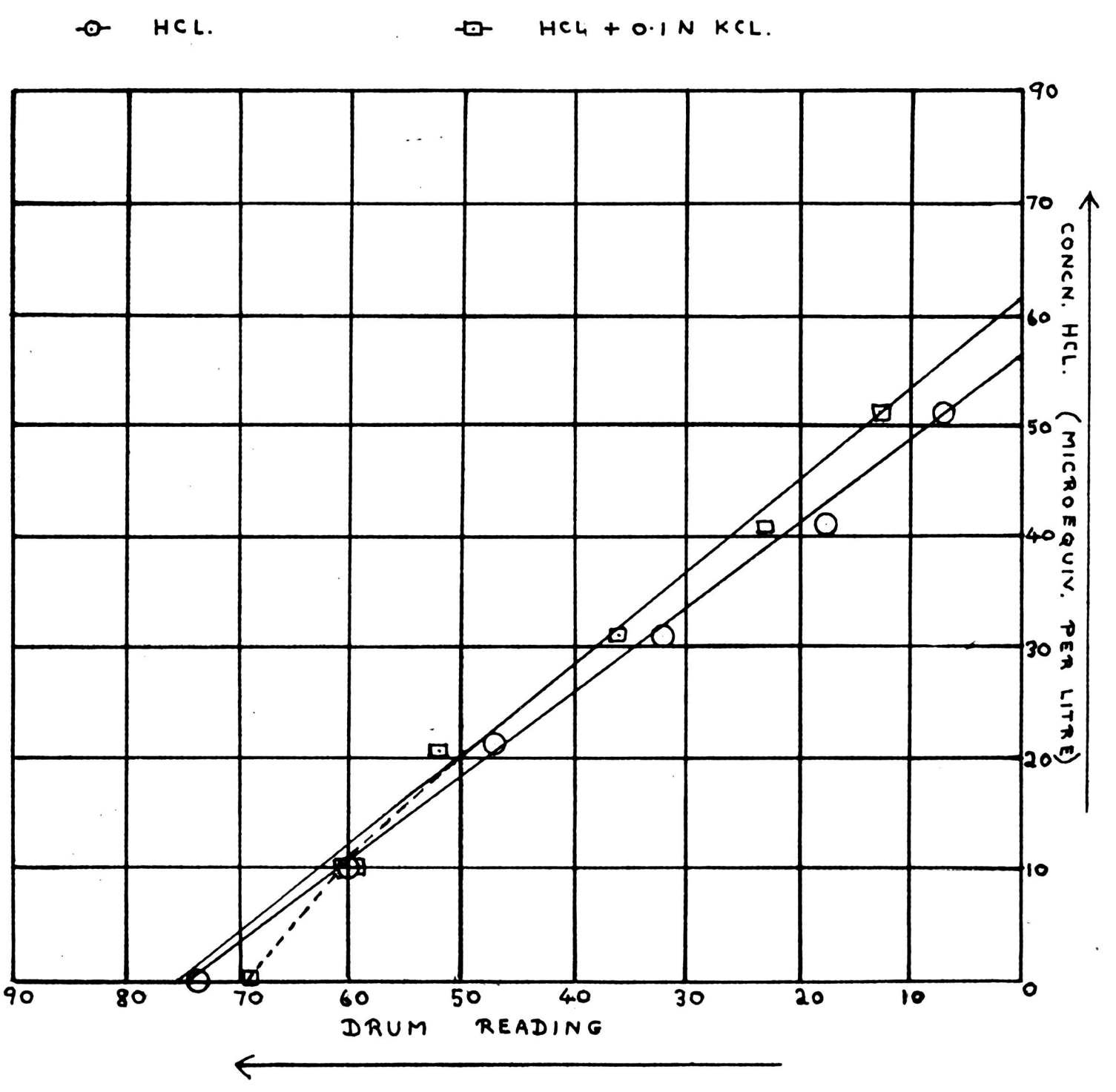
Table 8.

Calibration of Colorimeter.

Concn.HCl (micro-equiv.per litre)	Drum-readings.								
	A			B			C		
	1st. determ.	2nd. determ.	Mean	1st. determ.	2nd. determ.	Mean	1st. determ.	2nd. determ.	Mean
0.00	73.0	72.8		69.0	68.4		73.2	73.2	
	72.6	72.6		69.5	69.1		72.8	73.0	
	73.0	73.0		69.8	68.6		72.6	73.0	
	mean	mean		mean	mean		mean	mean	
	73.0	72.8	72.9	69.5	68.7	69.1	72.9	73.1	73.0
10.25	59.8	60.6		59.4	59.3		60.2	60.3	
	59.8	59.8		60.4	60.2		60.1	60.0	
	60.4	59.6		60.6	59.6		60.0	60.0	
	mean	mean		mean	mean		mean	mean	
	60.0	60.0	60.0	60.1	59.7	59.9	60.1	60.1	60.1
20.50	47.5	47.2		52.0	52.3		48.0	47.8	
	48.0	48.3		51.5	51.4		47.8	48.0	
	47.3	47.3		51.8	51.8		47.6	48.0	
	mean	mean		mean	mean		mean	mean	
	47.6	47.6	47.6	51.8	51.8	51.8	47.8	47.6	47.6
30.75	32.0	32.0		36.4	36.8		32.2	32.0	
	31.8	31.4		35.8	36.9		32.2	32.2	
	32.1	32.1		36.6	35.8		32.4	32.0	
	mean	mean		mean	mean		mean	mean	
	31.9	31.8	31.9	36.3	36.5	36.4	32.3	32.1	32.2
41.00	17.5	17.8		22.5	23.6		18.2	18.0	
	18.0	16.9		23.0	22.5		18.2	18.1	
	18.1	18.0		22.8	22.8		18.0	18.0	
	mean	mean		mean	mean		mean	mean	
	17.8	17.6	17.7	22.7	22.9	22.8	18.2	18.0	18.1
51.25	6.8	7.2		13.0	12.2		7.2	7.0	
	6.8	6.6		13.3	13.4		7.0	6.9	
	7.0	6.7		12.6	12.3		7.0	7.0	
	mean	mean		mean	mean		mean	mean	
	6.8	6.8	6.8	13.0	12.6	12.8	7.0	7.0	7.0

Fig. 11.

Calibration Curves for Colorimeter.



drum-reading were obtained with solutions prepared from a second batch of 0.0001025N HCl, freshly made up from the stock acid solution.

It will be seen from the table that the presence of potassium chloride is without influence on the drum-reading when the concentration is 0.02N or, of course, less than this.

Influence of Concentration of Potassium Chloride on the Amount of Acid liberated from L-Type Charcoal by Potassium Chloride.

The concentration of potassium chloride was varied over the range 0.02N to 2N.

The charcoal (from Batch L_2: prepared from U_5) used in these experiments sorbed 210 x 10^{-5} equivalents of sodium hydroxide per gm. charcoal (see Table 12, page 69).

The procedure was as follows. About 0.3 gm. of charcoal was weighed accurately into a pyrex tube of the type described on page 33, and 25 ml. of potassium chloride solution of the required concentration was added from a calibrated pipette. After the stopper was sealed on with paraffin wax, the contents of the tube were shaken for twenty-four hours on a slowly revolving wheel. At the end of this period, the charcoal was separated from the solution by centrifuging. A 1 ml. test sample of the centrifugate was diluted by a factor of 50 in

Table 9.

Relation between Potassium Chloride Concentration and Amount of Liberated Acid.

KCl concn. (N)	Weight of charcoal (gm.)	Dil^{n}. factor	Conc^{n}. KCl in diluted centrifugate (N)	Drum-readings 1	2	3	Mean	Conc^{n}. of acid in diluted centrifugate (microequiv. per litre)	H^{+} ion liberated per gm. charcoal (10^{-5} equiv.)	Mean
0.02	0.3009	50	0.0004	45.2	45.0	44.7	45.0	21.75	9.0	9.0
	0.3005			45.0	45.4	44.8	45.1	21.75	9.0	
0.10	0.3012	50	0.0020	41.5	42.0	41.0	41.5	24.25	10.1	10.0
	0.3020			41.8	42.3	41.5	41.9	24.00	9.9	
0.20	0.3002	50	0.0040	37.5	38.0	37.2	37.6	27.50	11.5	11.4
	0.3000			38.4	37.6	38.2	38.1	27.00	11.3	
0.50	0.3004	50	0.0100	31.4	32.0	31.5	31.6	32.00	13.3	13.3
	0.3000			31.8	32.4	32.2	32.1	31.75	13.2	
1.00	0.3002	50	0.0200	31.8	31.2	32.0	31.7	31.80	13.2	13.2
	0.3000			32.1	31.6	31.8	31.8	31.80	13.2	
0.00	0.3000	50	0.0000	51.6	51.4	51.4	51.5	16.75	1.4	1.4
	0.3000			51.4	51.0	50.9	51.1	17.00	1.4	

order that the acid content of the diluted centrifugate could be estimated from the calibration curve.

The data are recorded in Table 9 (page 63). From the 4th column it will be seen that the concentration of potassium chloride in the diluted centrifugate was never greater than 0.02N. Hence, in every case, the acid concentration could be derived from the hydrochloric acid calibration curve in Fig.11.

The results are discussed on page 109.

Effect of Variation in the Ratio :
Volume of Solution/Weight of Charcoal.

For reasons which are explained in the Discussion (page 109), it was decided to investigate the effect of varying the ratio

Volume of 1.0N potassium chloride solution/weight of charcoal

upon the liberation of acid. It was first thought that the required data might be obtained by keeping the weight of charcoal constant and increasing the volume of potassium chloride solution to values greater than 25 ml. Also, it was expected that with large volumes, the concentration of acid in the centrifugate would be so low that further dilution, to bring the concentration of salt from 1.0N to the

values at which the calibration curves in Fig.11 were obtained, would render the acid concentration too low for these curves to be applicable. Efforts were therefore made to obtain a calibration curve for systems containing 1.0N salt. Appropriate mixtures of HCl and 1.0N KCl were therefore prepared and examined in the manner previously described.

The results are given in Table 10 (below), and show that the method was not sufficiently sensitive with 1.0N KCl present. It may be added that the mixtures were yellow, whereas those containing 0.1N or 0.02N KCl were dark reddish-blue.

Table 10.

Calibration of Colorimeter with HCl - 1.0N KCl Mixtures.

Concentration HCl (microequiv. per litre)	Drum-readings					
	1	2	3	4	5	Mean
9.63	88	88	87	88	88	88
19.26	86	85	82	84	84	84
28.89	84	86	82	83	84	84
38.52	75	79	80	76	76	77

In view of the above, it became necessary to employ a volume of 1.0N KCl not greater than 25 ml. and to vary the weight of charcoal. It was then possible, by suitable dilution of the centrifugate, to use the calibration curves in Fig.11. Charcoal from Batch L_2 was again used.

Table 11.

Effect of Variation in the Ratio : Volume of Solution/Weight of Charcoal.

Expt. No.	Weight of Charcoal (gm.)	Volume of 1.0N KCl (ml.)	Dilution factor	Concentration KCl in diluted centrifugate (N)	Drum-readings						Concentration of acid in diluted centrifugate (microequiv. per litre).	H^+ ion liberated per gm. charcoal (10^{-5} equiv.)
					1	2	3	4	5	Mean		
1	1.0090	10	250	0.004	46	42	34	41	40	40	25.60	6.32
2	0.5091	10	150	0.007	42	41	43	41	42	42	24.00	7.10
3	0.6628	25	150	0.007	56	55	55	57	55	55	14.25	7.90
4	0.4004	25	50	0.020	24	25	26	25	25	25	37.00	11.70
5	0.3020	25	50	0.020	33	32	30	31	32	32	31.75	13.16
6	0.1432	25	25	0.040	38	37	40	37	37	38	27.00	11.80
7	0.1020	25	10	0.100	15	16	16	15	17	16	48.50	11.88

The data are recorded in Table 11 (page 66) and discussed in page 109.

Further Experiments.

A weighed amount of L-type charcoal (from Batch L_2) was treated with 25 ml. of 0.2N sodium hydroxide in the manner described on page 33. The suspension was centrifuged, and the centrifugate analysed to determime the amount of base sorbed by the charcoal. (Data in Table 12, page 69).

The charcoal thus separated from the bulk of the adsorbate was transferred to a sintered-glass filter (Schott-Jena 11G3), roughly dried by suction, and then washed continuously, using very gentle suction, with about 1600 ml. of distilled water. The washings were periodically tested with methyl red, and the last portions still gave an alkaline reaction.

After the washing treatment, the charcoal was air-dried for 8 hours by means of a water-pump attached to the sintered-glass filter (which was kept covered), placed in a sorption tube with 25 ml. of 0.1N hydrochloric acid, and the suspension shaken for 24 hours in the usual manner. At the end of this period, the contents of the tube were centrifuged, and the centrifugate titrated with 0.05N NaOH to determine the amount of acid which had been sorbed (Data in Table 13, page 69).

As before, the charcoal was next washed with 1600 ml. of distilled water, the final washings still showing an acid reaction to methyl red. The washed material was air-dried, placed in a sorption tube with 25 ml. of 1.ON potassium chloride solution and shaken for 24 hours. The acid content of the centrifugate from this suspension was determined colorimetrically as previously described (Data in Table 14, page 69).

The charcoal was again washed and dried and its capacity to sorb base then redetermined (Data in Table 15).

Since the initial base sorption of the charcoal was 210 x 10^{-5} equivalents NaOH per gm. (Table 12), the material could not be considered as being fully oxidised. Wilson and Bolam[1] have obtained sugar-charcoal which could sorb more than 300 x 10^{-5} equivalents NaOH per gm. Therefore it was possible that some of the acid sorbed by the charcoal during the hydrochloric acid treatment was taken up by a part of the surface similar to that responsible for the sorption of acid by an H-type charcoal. Consequently, it was decided to ascertain the amount of acid adsorbed by a sample L_2 charcoal, when treated with 0.1N HCl. The technique was similar to that used previously, and the data are given in Table 16.

The results of all these experiments are discussed on page 114.

Table 12.

Treatment with Sodium Hydroxide (0.2N).

Expt.	Weight of charcoal (gm.)	Change in titre on 10 ml. 0.2N NaOH (ml. 0.1N HCl)	Equivalents of NaOH sorbed per gm. charcoal ($\times 10^5$)
1	0.3003	2.52	210.5
2	0.3000	2.51	210.0

Table 13.

Treatment with Hydrochloric Acid (0.1N).

Expt.	Weight of charcoal (gm.)	Change in titre on 10 ml. 0.1N HCl (ml. 0.05N NaOH)	Equivalents of HCl sorbed per gm. charcoal ($\times 10^5$)
1	0.3003	0.90	75.25
2	0.3000	0.91	75.30

Table 14.

Treatment with ~~+~~ 0.1N Potassium Chloride.

Expt.	Weight of Charcoal (gm.)	Dilution factor	Drum-reading (Mean value)	H^+ ion liberated per gm. charcoal (10^{-5} equiv.)
1	0.3003	50	31.9	13.0
2	0.3000	50	31.4	13.2

Table 15.

Base-Sorption of Tri-treated Charcoal.

Expt.	Weight of Charcoal (gm.)	Change in titre on 10 ml. 0.2N NaOH (ml. 0.1N HCl)	Equivalents NaOH sorbed per gm. charcoal ($\times 10^5$)
1	0.2703	2.03	185.9
2	0.2700	2.01	185.3

Table 16.

Sorption of Acid by L-type Charcoal (Batch L_2).

Weight of Charcoal (gm.)	Change in titre on 10 ml. 0.1N HCl (ml. 0.05N NaOH)	Equivalents HCl sorbed per gm. charcoal ($\times 10^5$)
0.3002	0.12	4.5
0.3005	0.13	4.6

IV. ACTION OF L-TYPE CHARCOAL ON SODIUM ARSENITE.

Estimation of Sodium Arsenate in the Presence of Sodium Arsenite.

Since it was expected that the concentrations of sodium arsenate likely to be encountered in this series of experiments would be small, the feasibility of estimating arsenate, in the presence of arsenite, on a colorimetric basis was first examined. The reaction between an arsenate and a mixture of ammonium molybdate and stannous chloride was used as the basis of the estimation. It is reported[7] that a yellow colour is produced by arsenates, but not by arsenites, at least under certain conditions. However, experiment showed that, with the concentrations used in the present work, a yellow colour was given by arsenite, of an intensity such that a colorimetric estimation of arsenate in a mixture of arsenite and arsenate was rendered impossible.

Since the colorimetric method did not yield satisfactory results, it was decided to attempt the estimation on a gravimetric basis, according to the method of Lewis and Davis[8]. In this method, the sodium arsenite in the mixture is converted into sodium arsenate by oxidising with potassium bromate. The total arsenic is subsequently determined by forming the ammonium uranyl acetate complex

$NH_4UO_2AsO_4.nH_2O$, which has been shown by Puller[9] to be quantitatively precipitated by the addition of a uranyl salt solution to an arsenate solution containing an excess of ammonium ions. This precipitate is soluble in mineral acids, but completely insoluble in acetic acid, and can be obtained in granular form by precipitation from a hot solution of the arsenate. When the precipitate is strongly heated until all the arsenic is volatilised, a moss-green residue is left, consisting mainly of uranium oxide (U_3O_8). The residue readily dissolves in a few drops of concentrated nitric acid, yielding a yellow solution of uranyl nitrate, which on cautious evaporation and subsequent ignition, decomposes readily to give a black residue consisting wholly of uranium oxide (U_3O_8). This oxide is a convenient form in which to estimate uranium. It has been shown by Jolibois and Bousset[10] that only a very small fraction of the oxygen is lost even when the oxide is heated for three hours in vacuum at 1000°. Its stability in air at high temperatures has been confirmed by Lebeau[11].

This method was investigated, and the experimental accuracy ascertained, by quantitatively oxidising a known fraction of a sodium arsenite solution prepared from a known weight of pure arsenious oxide, with potassium bromate and then determining the arsenic by the gravimetric method.

In the following, an account is given of the procedure actually adopted, and of the results obtained.

Standardisation of the Analytical Method.

A decinormal solution of sodium arsenite was prepared from ANALAR arsenious oxide according to the method of Vogel[12]. Actually 2.4993 gm. of the oxide, which had been dried at 110° for two hours prior to weighing, was dissolved in 2N sodium hydroxide, and the solution diluted to 200 ml. Next, 1.0N hydrochloric acid was added until the solution was acid to litmus. The sodium arsenite solution was then transferred to a 500 ml. graduated flask and diluted accordingly.

Eight 10 ml. portions of this sodium arsenite solution were accurately measured into eight 100 ml. beakers by means of a calibrated burette, and the contents of each beaker titrated with ca. 0.1N potassium bromate solution. The eight titres are recorded in Table 17 (page 84), under Experiments A_1 and A_2 (see below).

Each oxidised solution was diluted to 150 ml. with distilled water, and 30 ml. of 4N ammonium hydroxide added. The solutions were then acidified with acetic acid, heated to boiling and 50 ml. (excess) of approximately 0.1N uranyl acetate added slowly to each. The resulting yellow precipitate was allowed to stand overnight to coarsen. It was

noticed that the complex frequently appeared in the colloidal condition, in which case difficulty was experienced in obtaining a form suitable for filtration. The solutions had to be heated several times before a proper degree of granulation was achieved.

For filtration, the eight beakers were divided into two groups of four (designated Experiments A_1 and A_2), and the precipitates from each group collected on the same filter-paper. "Schleicher and Schüll" 589 (Blue Band) 7 cm. filter-papers were found to be the most suitable.

After thorough washing, the filter-paper with precipitate was transferred to a weighed silica crucible, and heated until the carbon was burnt off and the arsenic volatilised. The residue was moistened with a few drops of concentrated nitric acid, and heated to constant weight. To avoid loss by spurting, it was found necessary to exercise great care in the initial stages of heating. The values for the final weight of residue per 10 ml. of arsenite solution, i.e., one fourth of the weight of residue actually obtained in the analysis, are given in Table 18 (page 86).

Since three molecules of $NH_4UO_2AsO_4.nH_2O$ are required to form one molecule of U_3O_8, it follows that one molecule of U_3O_8 corresponds to three atoms of arsenic, or 842.2 gm. U_3O_8 to 224.7 gm. arsenic.

In the last column of Table 18 are given the values of the weight of arsenic per 10 ml. arsenite solution as calculated on the above basis from the weights of U_3O_8 obtained in Experiments A_1 and A_2. These estimations of the arsenic in the given solution agree well with the value 0.03784 gm. (see last column of Table 17) derived from the weight of arsenious oxide used in preparing the solution. From this agreement it was concluded (a) that the arsenious oxide was pure enough for the present purpose, and (b) that the method of analysis would probably be sensitive enough: this indeed proved to be the case.

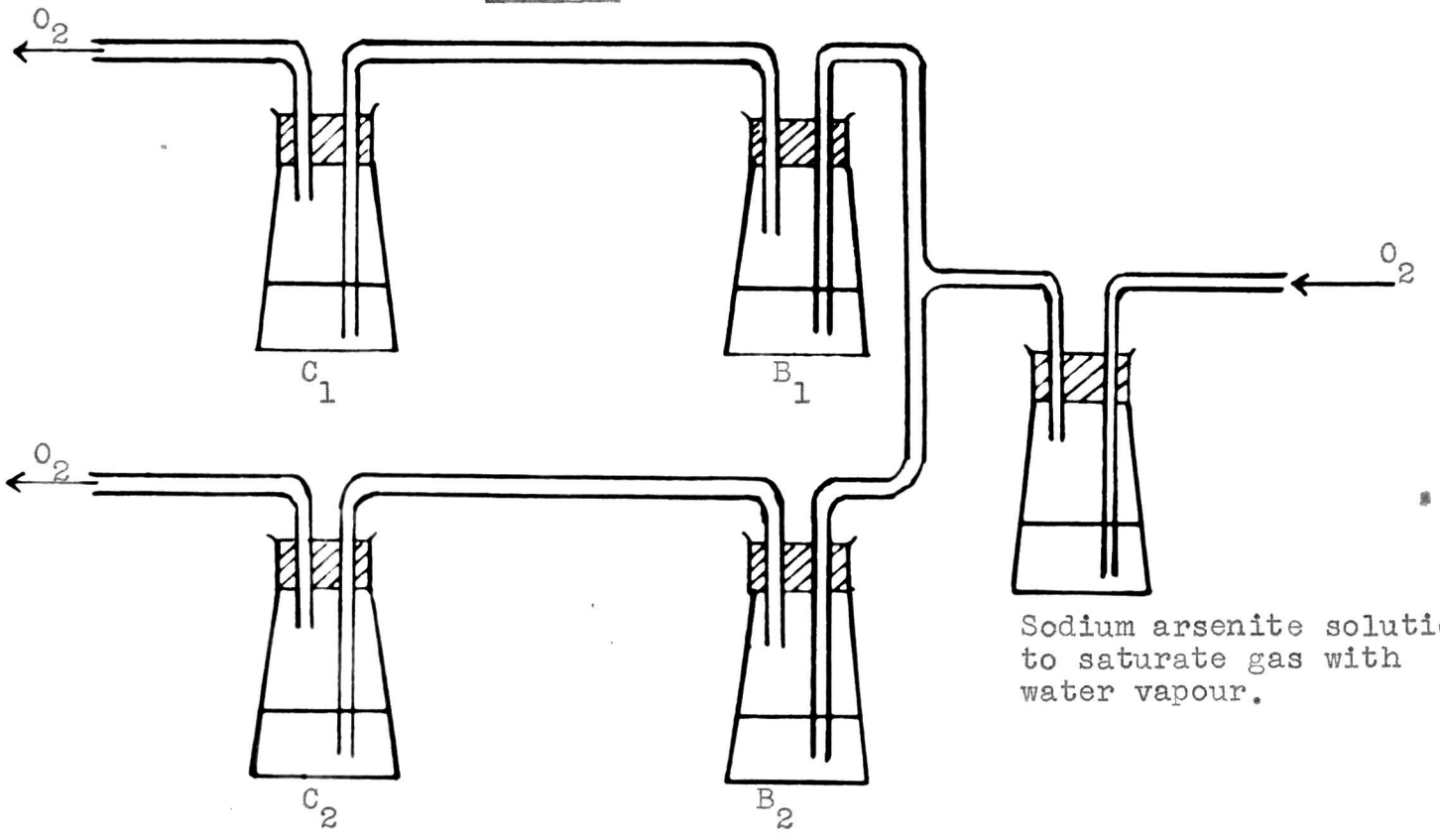
It will be seen from Table 17 (Experiments A_1 and A_2) that 10.12 ml. of the potassium bromate solution were equivalent to 0.03784 gm. of arsenic. This relation was used in the estimation of arsenic present as arsenite in subsequent experiments.

Treatment of Sodium Arsenite Solution with L-Type Charcoal in the Presence of Oxygen.

About 2 gm. of L-type charcoal (Batch L_3: prepared from U_6: base-sorption = 211 x 10^{-5} equiv. NaOH per gm.) was suspended in 25 ml. of decinormal sodium arsenite solution, and oxygen gas (cylinder) passed through the suspension at a rate of 3 bubbles per second for thirty minutes. After this treatment

Fig.12.

Fig.12.


O_2
C_1
B_1
O_2
O_2
C_2
B_2
Sodium arsenite solution
to saturate gas with
water vapour.

the solution was centrifuged free from the charcoal, two 10 ml. portions of the centrifugate were titrated with decinormal potassium bromate solution and the total arsenic content of each 10 ml. portion was separately determined by the gravimetric method.

A "blank" experiment was carried out at the same time with a solution from which the charcoal was absent. Both experiments were carried out in duplicate, those cases in which charcoal was present being termed Experiments C_1 and C_2 and the "blanks", Experiments B_1 and B_2.

The apparatus used is shown in Fig.12 (page 76). The results are recorded in Tables 17 and 18 (pages 84,85 and 86), and discussed on page 121.

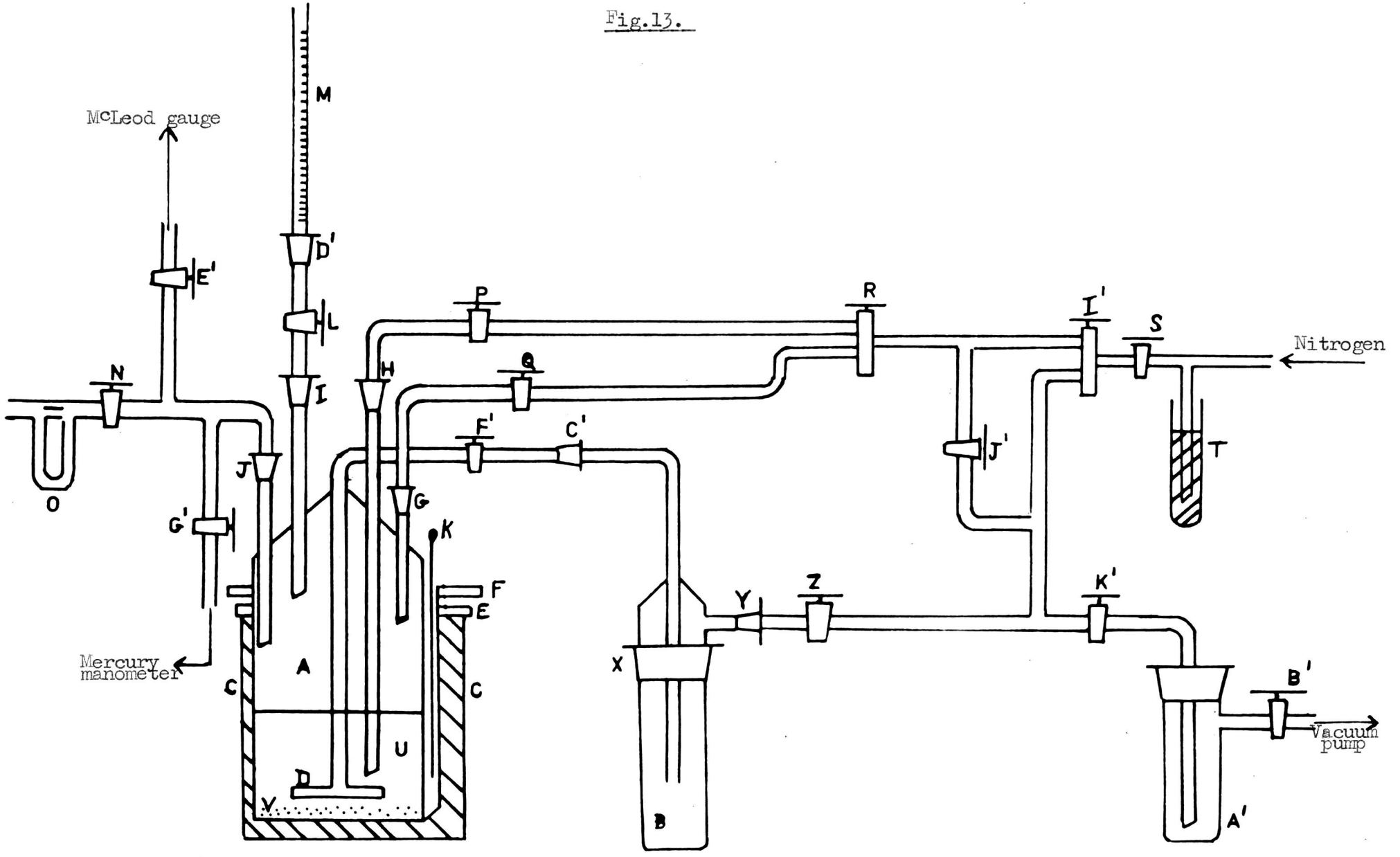
After centrifuging, the charcoal was washed with 500 ml. of distilled water, air-dried on a covered sintered-glass filter and the sorption of base redetermined by the usual procedure. The results will be found on page 123 of the Discussion.

Treatment of Sodium Arsenite Solution with L-Type Charcoal in the Absence of Oxygen.

In these experiments care was taken to exclude from the system, oxygen other than that chemisorbed on the charcoal. To this end, the apparatus shown in Fig.13 (page 78) was constructed, in order that the solution of sodium arsenite could be brought into contact with L-type charcoal from which

Fig.13.

Fig.13.


McLeod gauge
M
D'
E'
L
P
R
I'
S
Nitrogen
N
I
H
Q
F'
C'
J'
T
J
O
G
G'
K
F
E
Mercury manometer
A
C
C
U
D
V
X
Y
Z
K'
B'
Vacuum pump
B
A'

Key to Fig.13.

A. Pyrex reaction vessel; 100 ml. capacity.

B. Sampling flask; 100 ml. capacity.

C. Electric furnace.

D. Sintered-glass disc

E. Asbestos baffle.

F. Aluminium foil.

J, H, G, C', Y. "Quick-fit" A.7 cones and sockets.

D', I. "Quick-fit" B.10 cones and sockts.

K. Thermometer.

E', N, L, P, Q, S, Z, B', F', G', J', K', Pyrex taps (2 mm. bore).

M. Burette; 10 ml.

O. Mercury flowmeter.

R, I'. Two-way pyrex taps (3 mm. bore)

T. Mercury blow-off valve.

U. Sodium arsenite solution.

V. Charcoal.

X. "Quick-fit" B.24 cone and socket.

A'. Liquid-air trap.

physically adsorbed oxygen had been removed, by heating the charcoal in vacuum at 200° for 1 hour. Agitation of the suspension was effected by a stream of commercial oxygen-free nitrogen. As before, the charcoal and solution were kept in contact for thirty minutes. A sample of the solution was then withdrawn from the reaction vessel, filtered free from charcoal by passage through a sintered-glass disc, and analysed. At no time during the sampling did the charcoal suspension come into contact with the air. The experimental procedure is described below.

About 2 gm. of L-type charcoal (from Batch L_3) was introduced into the reaction vessel A through I, and M and L placed in position. The taps P, F', L and N were closed, and A evacuated through taps Q, R, J', K' and B' by means of a "Speedivac" pump. When the pressure in the apparatus was low, as indicated by a McLeod gauge, the furnace was allowed to heat up to 200°, and evacuation of the charcoal continued under these conditions for one hour.

The furnace was now removed and the reaction vessel allowed to cool for one hour. Taps B', K' and J' were then closed, S fully opened, tap I' turned to R and R slowly turned to Q, so that nitrogen entered the reaction vessel until the

pressure in A was a little greater than atmospheric. Then taps G' and E' were closed, N opened and the nitrogen allowed to escape through the flowmeter O. The passage of nitrogen was continued for 30 minutes, after which taps N, Q, R, I' and S were closed.

The burette M was filled with decinormal sodium arsenite solution; Z, F', K' and B' opened and the pressure in A allowed to decrease by a small amount. With these taps closed, L was opened long enough to allow a known volume of solution to be introduced into A. Nitrogen was passed through the charcoal suspension for thirty minutes, and a sample (20 ml.) of the solution then withdrawn, via the sintered-glass disc D, into the sampling tube B, by the application of nitrogen pressure through Q. Two 10 ml. portions of the sample were analysed for arsenite by titration with the standardised potassium bromate solution.

After the withdrawal of the sample, tap F' was closed, and the damp charcoal left under partial vacuum in A. A known volume of distilled water was added to the charcoal from the burette M in the same manner as for the addition of sodium arsenite solution. After contact with the charcoal, the wash-water was withdrawn into the sampling tube. This procedure was repeated until the charcoal had been

washed with 500 ml. of water (in 50 ml. portions). Any residual wash-water adhering to the charcoal was evaporated by keeping A under vacuum and applying a little heat.

A known volume of 0.2N sodium hydroxide was now added to the charcoal from the burette M. Nitrogen was bubbled through the suspension for 24 hours, after which a sample of the sodium hydroxide was withdrawn for analysis. Two 10 ml. portions of the sample were titrated with decinormal hydrochloric acid.

The results of these experiments (D_1 and D_2) are recorded in Table 17 (page 85) and on page 122 of the Discussion.

The Influence of Sodium Arsenite Concentration.

About 2 gm. of L-type charcoal (from Batch L_3) was suspended in 25 ml. of about 0.4 molar sodium arsenite solution, and oxygen gas bubbled through the suspension at a rate of 3 bubbles per second for 30 minutes. At the end of this time, the solution was centrifuged free from charcoal and two 10 ml. portions of the centrifugate titrated with standardised potassium bromate solution.

A "blank" experiment was carried out at the same time from which the charcoal was absent. Both experiments were carried out in duplicate, those cases

in which the charcoal was present being termed Experiments E_1 and E_2, and the "blanks", Experiments F_1 and F_2. The apparatus used is shown in Fig.12 (page 76) and the results are recorded in Table 17 (page 85).

After centrifuging, the charcoal was washed with 500 ml. of distilled water, air-dried on a covered sintered-glass funnel and shaken with 25 ml. of 0.2N sodium hydroxide solution for 24 hours. The amount of sodium hydroxide sorbed by the charcoal was determined as described in page 33. The results are given on page 123 of the Discussion.

Table 17.

Estimation of Arsenic present as Arsenite.

Expt.	Initial conc^{n}. of arsenite sol^{n}. (moles per litre)	Conditions	Volume $KBrO_3$ required for 10 ml. sol^{n}. (ml.)	Mean	Weight of arsenic as arsenite in 10 ml. sol^{n}. (gm.)
A_1	0.0506	Stock soln. of sodium arsenite	10.10 10.10 10.12 10.11	10.11	0.03784
A_2	0.0506	"	10.10 10.14 10.14 10.10	10.12	"
B_1	0.0506	Soln. treated with oxygen alone	10.16 10.12	10.14	0.03792
B_2	0.0506	"	10.18 10.18	10.18	0.03806
C_1	0.0506	Soln. treated with charcoal and oxygen	8.18 8.17	8.18	0.03060
C_2	0.0506	"	8.12 8.15	8.14	0.03045

Table 17 (continued).

Expt.	Initial conc^{n}. of arsenite sol^{n}. (moles per litre)	Conditions	Volume $KBrO_3$ required for 10 ml. sol^{n}. (ml.)	Mean	Weight of arsenic as arsenite in 10 ml. sol^{n}. (gm.)
D_1	0.0506	Soln. treated with charcoal in absence of oxygen	8.22 8.20	8.21	0.03070
D_2	0.0506	"	8.10 8.12	8.11	0.03033
E_1	0.3864	Soln. treated with oxygen alone	77.10 77.70	77.40	0.2895
E_2	0.3864	"	77.60 77.70	77.65	0.2905
F_1	0.3864	Soln. treated with charcoal and oxygen	48.00 48.20	48.10	0.1799
F_2	0.3864	"	48.20 48.00	48.10	0.1799

Table 18.

Estimation of Total Arsenic.

Experiment	Conditions	Weight of U_3O_8 from 10 ml. solution (gm.)	Weight of total arsenic in 10 ml. solution. (gm.)	Mean
A_1	Stock solution of sodium arsenite	0.1408	0.03758	
A_2	"	0.1418	0.03783	0.03771
C_1	Solution treated with charcoal and oxygen	0.1271	0.03390	
		0.1290	0.03442	0.03416
C_2	"	0.1301	0.03470	
		0.1308	0.03489	0.03480

V. INTERACTION BETWEEN CHARCOAL AND GRIGNARD REAGENT.

Preparation of Grignard Reagent (Methyl Magnesium Iodide).

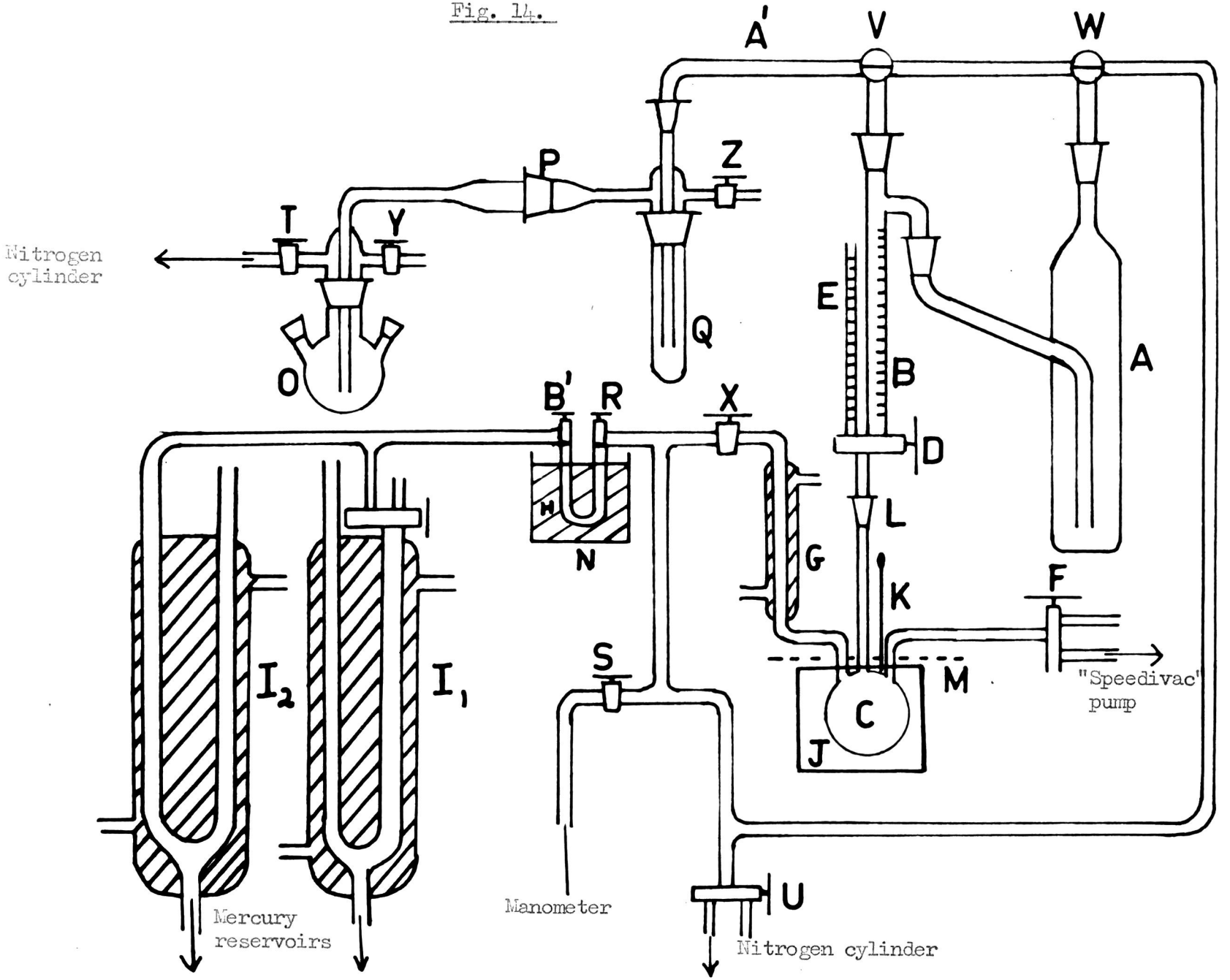
Altogether four solutions of the reagent were prepared.

Preparations I and IV. 100 Gm. of di-isoamyl ether (Hopkin and Williams, or Eastman Kodak) and 12 gm. of magnesium turnings (Hopkin and Williams) were placed in a three-necked flask (1 litre) fitted with a reflux condenser, a stirrer and a dropping funnel. A solution of 60 gm. of methyl iodide in 50 gm. of di-isoamyl ether was added, with constant stirring and so slowly that the mixture was kept below 20°. After the final addition, the mixture was heated on a water-bath for 2 hours, allowed to cool to room temperature, and diluted with 270 gm. of di-isoamyl ether. Excess of methyl iodide was removed by distillation on a water-bath. Throughout the procedure air was excluded by passing commercial oxygen-free nitrogen through the apparatus.

Preparation II. In this case the final addition of di-isoamyl ether was omitted in an attempt to obtain a high concentration of methyl magnesium iodide. This resulted in much of the reagent appearing in a permanently colloidal form, and it could not be

Fig.14.

Fig. 14.


A'
V
W
P
Z
T
Y
Nitrogen cylinder
O
Q
E
B
A
B'
R
X
D
H
N
L
G
K
F
S
M
"Speedivac" pump
C
J
I_2
I_1
Mercury reservoirs
Manometer
U
Nitrogen cylinder

redissolved by subsequent addition of ether.

Preparation III. 100 Ml. of di-isoamyl ether was added in the final addition, as against 270 ml. in the case of Preparations II and IV. Some colloidal material was still produced, but on standing for a few days the solid settled out, and a clear solution of methyl magnesium iodide could be decanted off.

The Apparatus.

The apparatus used for investigating the interaction of charcoal with Grignard reagent is shown in Fig.14 (page 88). It was a modified form of that used by other workers[13,14,15] for the estimation of active hydrogen in organic compounds.

The 1000 ml. cylindrical reservoir A, used for storing the reagent, was connected to the 10 ml. burette B (graduated in tenths of a ml.), from which reagent could be added to the 50 ml. round-bottomed flask C, which acted as the reaction vessel. C could be connected, by means of the two-way tap D, to B, or to the 5 ml. burette E (graduated in hundredths of a ml.) when it was desired to add water to the reaction vessel. The vessel was furnished with two side-arms, one providing for connection to a "Speedivac" pump (attached to the two-way stopcock F) and the other for connection, via a water condenser G and the U-tube H (containing phosphorus pentoxide), to the water-jacketed 50 ml. gas

burettes I_1 and I_2.

When heating at 100° or 181° was required, the reaction vessel was enclosed in the small portable electric heater J (in the form of a hollow cylinder). The current through J was regulated, by means of a rheostat, to keep the temperature within ±1° of the desired value, as indicated by the thermometer K. The neck of C was made specially long to reduce heating-up of the joint L by radiation from J. For the same purpose, a stream of cold air was directed on L from an air-compressor, and asbestos lagging provided at M.

The P_2O_5 tube H was kept immersed in a small water-bath N, maintained at 20° by means of water circulated from a large water-thermostat. When it was necessary to bring the contents of C to 20°, it was possible to move N, still containing H, to such a position that the bulb of the reaction vessel was also immersed.

Parts O, P and Q were employed solely when transferring reagent from the preparation flask to the reservoir A, and were disconnected after use. Taps (of the vacuum type where necessary) and ground-glass joints were lubricated with Apiezon-L grease (Edwards).

Transfer of Grignard Reagent to the Apparatus.

Grignard reagent was transferred from the flask in which it was prepared to the reservoir A by the following procedure, designed to minimise contact of the solution with atmospheric oxygen and moisture.

Flask O (of the same size as the preparation flask), tube P, packed with glass wool, and the settling tower Q were assembled as shown in the diagram. The air was then displaced from the apparatus (up to taps R and S) by passing a rapid stream of commercial oxygen-free nitrogen for several hours. The gas was admitted at T and allowed to escape at tap F or tap U by suitable manipulation of these and of the taps V, W (both 3-way, 90°), D and X.

When the sweeping was complete, D. U, V and W were closed and flask O quickly replaced by the flask containing the reagent, access of air being prevented by a stream of nitrogen, entering at T and U and escaping at Y. The reagent was then passed through the filter P into Q by forcing nitrogen in at T, Z being opened to the air and Y closed. After the reagent had been allowed to stand in Q until clear it was driven (by nitrogen) into the reservoir A by closing Z, opening U to the air and turning V to connect Q with B, and W to connect A with U, where the displaced nitrogen escaped. After all the

solution had been transferred, the nitrogen was stopped, stopcocks V and W were closed, and O, P and Q removed.

Standardisation of the Reagent Solution.

Before use, the reagent was standardised, i.e., determination was made of the volume (at N.T.P.) of methane liberated when the reagent in one ml. of solution was completely decomposed by reaction with water. The following procedure was adopted.

(i) Transfer of reagent to burette B. Taps S, R and X were closed, W was turned to connect A with U, and V turned to connect B with A' (now open to the air), D being closed. Nitrogen was admitted at U and, passing through W, forced reagent from A into B, the nitrogen displaced from B passing out of the apparatus through V. When B was full the nitrogen stream was stopped and taps V, W and U closed.

(ii) Removal of moisture from reaction vessel. The reaction vessel C, after careful cleaning, was placed in position and evacuated by closing tap R, opening taps S and X and pumping out through F. The pressure in C was recorded by the manometer attached at S. When a suitable vacuum was obtained, C was heated to 181° and maintained there (by means of the heater J) for one hour. At the end of this period the heater was switched off and C allowed to cool. The vacuum

was maintained throughout these operations.

This treatment ensured that all traces of moisture were removed from the walls of the reaction vessel. When C was cold the pump was switched off, S closed, nitrogen admitted at U and allowed to stream through C to escape at F. X, F and U were subsequently closed and the nitrogen turned off.

(iii) Reaction between Grignard reagent and water.

The air in the burette system (to the left of tap R) was displaced by nitrogen (admitted at U), the mercury levels adjusted and tap X opened (S, U and F being closed). C and H were brought to 20° by immersion in water-bath N and the initial burette reading noted on I_1, the mercury level in the other burette I_2 being at a suitable position, to which it was returned when the second reading of I_1 was taken. Burette I_2 allowed for expansion when C was heated to 100° or 181°. The temperature of the gas-burettes and the atmospheric pressure were recorded.

The mercury reservoirs attached to the gas-burettes were lowered to create a partial vacuum in C, and a measured quantity of reagent added to C from B. With the partial vacuum still maintained, excess of water was now added to C from the burette E.

The water-bath N was replaced by the heater J,

the reaction mixture heated up to 100° and maintained at this temperature for about 30 minutes, by which time reaction between the reagent and water had ceased. Then C (by immersion in N) was brought back to 20°, and the final reading on I_1 noted, together with the temperature of the gas-burette and the atmospheric pressure. The difference in the readings of burette I_1 gave the total increase in volume of the system. To obtain the volume of methane produced by the reaction, it was necessary to subtract the volumes of reagent and water added. The volume (at N.T.P.) of methane produced when the reagent in one ml. of solution was decomposed with excess of water could now be calculated.

The experimental data are recorded in Table 19 (page 98).

Interaction between Grignard Reagent and Charcoal.

In these experiments a known volume of standardised Grignard reagent solution was heated at 181° with a known weight (ca. 0.5 gm.) of charcoal for a definite period of time and determination made of the volume of gas evolved. The reaction mixture was then heated at 100° with a known volume of water and again the resulting volume of gas measured. These two distinct parts of the procedure may be conveniently referred to as the first and second

stages, respectively, of the experiment. In some cases observation was made of the rate of evolution of the gas during the first stage. Experiments were carried out with both L-type and H-type charcoals, under comparable conditions. The actual procedure is described in the following.

(i) Desorption of water from the charcoal. An accurately known weight of charcoal was placed in the reaction vessel C, care being taken to ensure that no solid remained adhering to the long neck of the flask. The vessel was then connected to the rest of the apparatus and slowly evacuated. If the evacuation was carried out too quickly, some charcoal was withdrawn into the pump line. When the pressure in C became very low, the portable heater was placed in position, and the temperature slowly raised to 181°, and kept at that value for one hour, the evacuation being continued. This ensured the removal of any physically adsorbed water from the charcoal surface. The reaction vessel was now allowed to cool in a slow stream of nitrogen, admitted at U; the gas in the vessel finally attaining atmospheric pressure. There was a tendency for the charcoal to be ejected from the bulb of the flask into the neck if the nitrogen was admitted rapidly.

(ii) First stage of experiment. The gas-burettes were adjusted (with the reaction vessel at 20°) to

obtain the first reading of I_1, and a measured quantity of reagent added to the charcoal, as described under (iii) on page 94 . The mixture of charcoal and reagent was now heated at 181° for a known time, and then brought back to 20°. When equilibrium had been established, the second reading of I_1 was taken (see (ii) on page 93).

(iii) Second stage of experiment. The second burette reading obtained as described above was used as the initial burette reading in the second stage of the experiment, in which the procedure was that described under (iii) on page 93 for the reaction between Grignard reagent and water.

It should be added that in the experiments involving long periods of heating at 181°, it was necessary to employ 3 or 4 burettes to cope with the volume of gas to be measured.

The data obtained in these experiments are recorded in Tables 21 and 22 (pages 101 - 103).

Further Experiments.

(a) Treatment of Charcoal with Isoamyl Ether.

Experiments were carried out, with both L-type and H-type charcoals, in which the charcoal was heated with isoamyl ether alone. Exactly the same procedure was employed as in the study of the charcoal-Grignard reagent systems, except that the ether was added directly to the burette B. The results

obtained in these experiments will be found in Table 22 (page 103).

(b) Thermal Decomposition of Grignard Reagent.

A few experiments were performed to ascertain how far decomposition of the reagent, to give gaseous products, occurred when heated at 181°. The relevant data are contained in Table 19 (page 98).

(c) Sorption of Base by Charcoal after Treatment.

In some of the experiments, the charcoal was recovered after treatment with Grignard reagent or isoamyl ether, and the sorption of base redetermined. After treatment with Grignard reagent, the charcoal was much contaminated with magnesium hydroxide. This was dissolved out by addition of 200 ml. of 4N HCl. The charcoal was then thoroughly washed with 500 ml. of water and air-dried, in the fashion described on page 77 , and the sorption from 0.2N NaOH determined in the usual manner. Charcoal which had been treated with isoamyl ether only was subject to exactly the same treatment with HCl etc., to keep conditions comparable. The results of these experiments are shown in Table 23 (page 104).

67

Table 19.

Grignard Reagent Alone.

Grignard reagent Preparation No.	Volume of reagent (ml.)	Time of heating during 1st stage (hours)	Volume of gas evolved (c.c.at N.T.P.)					
			1st Stage		2nd Stage		Total	
				mean		mean		mean
I	10	2	4.40 5.96	5.18	20.70 21.34	21.02	25.10 27.30	26.20
		5	9.71 -	9.71	13.21 -	13.21	22.92 -	22.92
II	4	0	- - - -	-	84.45 86.71 85.20 85.47	85.46	- - - -	-
III	10	0	- -	-	65.60 65.71	65.66	- -	-
			- -	-	62.21 59.95	61.08	- -	-
		5	22.32 19.26	20.79	29.43 30.36	29.90	51.75 49.62	50.69
IV	10	0	- -	-	66.97 66.81	66.89	- -	-
			- -	-	115.84 -	115.84	- -	-
		5	14.05 13.69	13.87	40.41 39.73	40.07	54.46 53.42	53.94
		0	- -	-	65.69 -	65.69	- -	-

Table 20.

Grignard Reagent + Charcoal.

Grignard reagent Preparation No.	Volume of reagent (ml.)	Time of heating during 1st stage (hours)	Expt. No.	Charcoal	Volume of gas evolved (c.c.at N.T.P.)					
					1st Stage		2nd Stage		Total	
						mean		mean		mean
I	10	2	1a	L_3	20.00 18.15	19.08	13.94 14.37	14.16	33.94 32.52	33.23
			1b	H_4	12.76 12.80	12.78	18.71 20.23	19.47	31.47 33.03	32.25
		5	2a	L_3	26.19 26.50	26.35	0.55 1.87	1.21	26.74 28.37	27.56
			2b	H_4	14.99 -	14.99	11.99 -	11.99	26.88 -	26.88
II	4	2	3a	L_3	11.90 12.12	12.01	74.73 76.44	75.59	86.63 88.56	87.60
			3b	H_4	9.99 11.00	10.50	79.61 74.43	77.02	89.60 85.43	87.52

Table 20 (continued).

Grignard Reagent + Charcoal.

Grignard reagent Preparation No.	Volume of reagent (ml.)	Time of heating during 1st stage (hours)	Expt. No.	Charcoal	Volume of gas evolved (c.c.at N.T.P. 1st Stage	mean	2nd Stage	mean	Total	mean
III	10	2	4a	L_3	22.22 22.22	22.22	42.23 42.48	42.36	64.45 64.70	64.58
			4b	H_4	17.97 17.35	17.66	46.76 46.75	46.76	64.73 64.10	64.42
		5	5a	L_3	(38.23) 37.72 36.86	37.29	(20.20) 15.10 16.81	15.96	(53.43) 58.82 53.67	53.29
			5b	H_4	22.27 20.70	21.49	31.59 32.36	31.98	53.86 53.06	53.46
IV	10	2	6a	L_4	22.68 22.81	22.75	34.16 32.78	33.47	56.84 55.59	56.22
			6b	H_5	18.62 17.77	18.20	36.41 36.14	36.38	55.03 53.91	54.48
		7	7a	L_3	41.33 41.84	41.59	12.97 14.03	13.50	54.30 55.87	55.09
			7b	H_4	25.63 26.25	25.94	29.32 28.21	28.77	54.95 54.46	54.71

Table 21.

Grignard Reagent + Charcoal (First Stage).

Time (hours)	Experiments.							
	5a				5b			
	1st determination		2nd determination		1st determination		2nd determination	
	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)
1.00	5.5	-	17.0	-	14.5	-	-	-
1.25	8.0	2.4	18.5	1.5	-	-	-	-
1.50	10.7	5.0	-	-	-	-	13.0	-
2.00	14.2	8.3	-	-	16.2	1.6	14.2	1.1
2.50	16.0	10.1	-	-	17.1	2.5	14.8	1.7
2.75	17.0	10.8	-	-	-	-	-	-
3.00	18.0	11.8	-	-	18.0	3.3	15.4	2.3
3.50	19.9	13.6	30.6	13.1	18.7	4.0	16.0	2.8
3.75	20.3	13.9	-	-	-	-	-	-
4.00	21.2	14.8	31.4	13.8	-	-	-	-
4.25	21.5	15.0	-	-	19.8	5.0	-	-
4.50	21.7	15.2	32.0	14.3	20.2	5.4	17.4	4.2
4.75	22.2	15.7	-	-	-	-	-	-
5.00	22.4	15.9	-	-	-	-	17.8	4.6

Table 21 (continued).

Grignard Reagent + Charcoal (First Stage).

Time (hours)	Experiments.							
	7a				7b			
	1st determination		2nd determination		1st determination		2nd determination	
	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)	Burette reading (ml.)	V at N.T.P. (ml.)
1.0	6.9	-	9.7	-	18.3	-	14.4	-
1.5	12.3	5.2	14.6	4.7	19.8	1.4	15.6	0.5
2.0	15.7	8.4	17.8	7.7	20.8	2.4	16.5	2.0
2.5	17.7	10.3	20.0	9.8	-	-	17.2	2.7
3.0	19.5	12.0	21.7	11.4	22.2	3.8	17.9	3.3
3.5	21.6	14.1	23.6	13.2	-	-	18.7	4.1
4.0	22.9	15.3	25.1	14.6	23.8	5.2	19.7	5.1
4.5	23.7	16.0	25.8	15.2	24.5	5.9	20.3	5.6
5.0	24.4	16.7	26.5	15.9	25.3	6.7	22.0	7.2
5.5	-	-	-	-	26.2	7.5	-	-
6.0	25.8	18.0	28.1	17.5	27.0	8.3	23.4	8.5
6.5	-	-	-	-	-	-	-	-
7.0	27.2	19.4	29.4	18.6	28.2	9.4	24.3	9.4

Table 22.

Isoamyl Ether + Charcoal.

Time of heating of 1st stage (hours)	Volume of ether (ml.)	Charcoal	Volume of gas evolved (c.c. at N.T.P.)					
			1st Stage		2nd Stage		Total	
				Mean		Mean		Mean
5	10	no charcoal present	2.69 1.77	2.23	- -	-	2.69 1.77	2.23
2	10	L_3	8.19 8.33	8.26	0.00 0.00	0.00	8.19 8.33	8.26
		H_4	8.79 8.40	8.60	0.00 0.00	0.00	8.79 8.40	8.60
2	10	L_4	9.02 8.18	8.60	- -	-	- -	-
5	10	L_4	8.65 10.19	9.42	- -	-	- -	-

Table 23.

Sorption of Base after Treatment with Grignard Reagent or Isoamyl Ether.

Reference	Liquid phase	Time of heating during 1st stage (hours)	Charcoal	Change in titre on 10 ml. of 0.2N NaOH (ml. 0.1N HCl)		Equivalents of base sorbed per gm. charcoal (10^{-5} equiv.)
					mean	
Table 20 Expt.4a	Grignard reagent III	2	L_3	2.39 2.37	2.38	120
Table 20 Expt. 5a	Grignard reagent III	5	L_3	1.69 1.67 1.64 1.64	1.66	83
Table 20 Expt. 6a	Grignard reagent IV	2	L_4	2.03 1.99	2.01	101
Table 20 Expt. 7a	Grignard reagent IV	7	L_3	1.51 1.49 1.53 1.54	1.52	76
Table 22	Isoamyl ether	2	L_4	1.92 1.89	1.91	96
Table 22	Isoamyl ether	5	L_4	1.29 1.27	1.28	64

(d) Analysis of Gas evolved in First Stage.

Samples of gas were analysed by means of the Bone and Wheeler apparatus[16]. The data are recorded in Table 24 (page 106). Experiments 1, 2, 3 and 4 were separate experiments, in which the charcoal and Grignard reagent were heated at 181° for 7 hours. At the end of this period, the suspension was cooled to 20°, a 50 ml. sample of gas withdrawn from the reaction vessel, and duplicate determinations of the gas composition carried out.

Table 24.

Analysis of Gas evolved in First Stage.

Expt. No.	Charcoal	C_2H_6 (%)		CH_4 (%)		N_2 (%)		Total (%)
1	L_4	5.3	mean	16.3	mean	78.4	mean	
		-		-		-		
			5.3		16.3		78.4	100.0
2	L_4	4.6		17.9		77.3		
		5.0		18.3		76.5		
			4.8		18.1		76.9	99.8
3	H_5	5.4		3.1		91.7		
		5.6		2.6		91.5		
			5.5		2.9		91.6	100.0
4	H_5	5.8		6.4		87.9		
		6.0		5.4		88.6		
			5.9		5.9		88.3	100.1

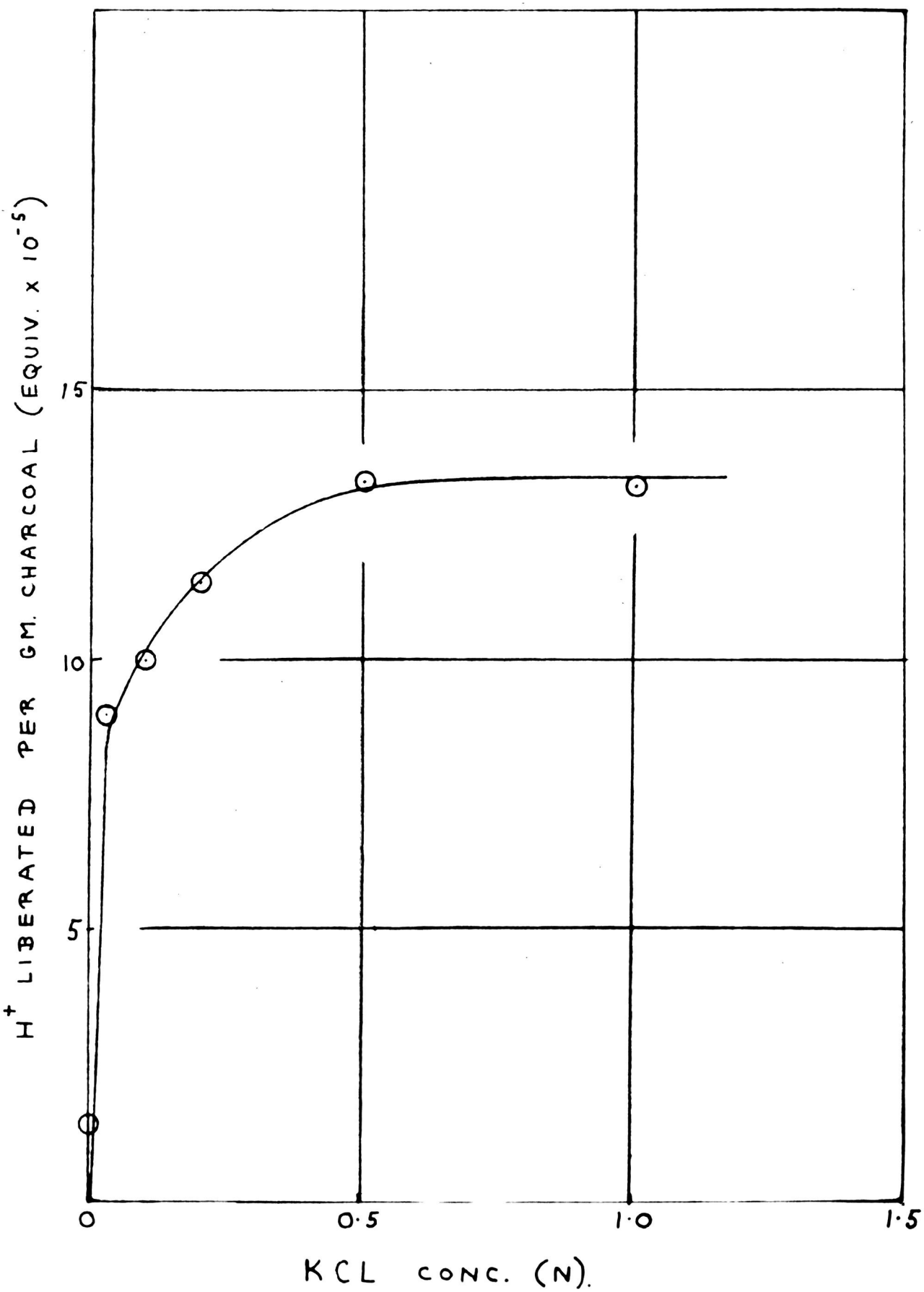
DISCUSSION.

Action of Neutral Salt on L-Type Charcoal.

If the oxygen responsible for base sorption is present as carboxyl or phenolic hydroxyl groups on the charcoal surface, then the hydrogen ions from such groups should undergo exchange when the charcoal is suspended in a solution of neutral salt. Under appropriate conditions, the maximum exchange should be equivalent to the maximum amount of base sorbed by the charcoal.

King[17] found that hydrogen ions were liberated when an L-charcoal was suspended in a solution of potassium chloride. The charcoal used in his experiments could sorb at least 200×10^{-5} equivalents NaOH per gm., and it was found that 1.98×10^{-5} equivalents acid per gm. were liberated by 0.02N potassium chloride, the single concentration studied. Thus, the amount of liberated hydrogen ion was only about 1 per cent. of the amount of base sorbed, but the concentration of potassium chloride used was low, and King does not indicate in his work whether equilibrium had been attained. In general, ion exchange increases with increase in neutral salt concentration, and a series of experiments was therefore carried out, covering a wide range of potassium chloride concentrations. The data are recorded in Table 9 (page 63) and graphed in Fig.15 (page 108).

Fig.15.


H+ LIBERATED PER GM. CHARCOAL (EQUIV. x 10-5)
15
10
5
0
0·5
1·0
1·5
KCL CONC. (N).

It will be seen that the maximum value of hydrogen ion liberated per gm. charcoal is 13×10^{-5} equivalents and that the exchange remains constant at this value over the range of salt concentrations 0.5 - 1.0N. While the value is considerably higher than King's, it is still far short of 210×10^{-5} equivalents, which is the maximum amount* of base sorbed per gm. of the charcoal used in these experiments.

However, it could be the case that the "concentration" of charcoal was too high to permit of maximum exchange. If the hydroxyl groups on the surface are weakly acidic, their tendency to ionise will decrease with increase in the concentration of liberated acid. Thus, when the exchange had attained 13×10^{-5} equivalents per gm. charcoal, the concentration of acid might conceivably be sufficient to suppress the ionisation of possible remaining acid groups. This effect has been observed by Achar and Usher[19], and by Bolam and Duncan[20], in the case of colloidal stearic acid. Experiments were therefore carried out, in which the concentration of potassium chloride was kept constant at 1.0N, and the ratio of the mass of

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*Previous work[1,18] has shown that the maximum sorption is attained with 0.2N sodium hydroxide, the concentration employed throughout the present work.

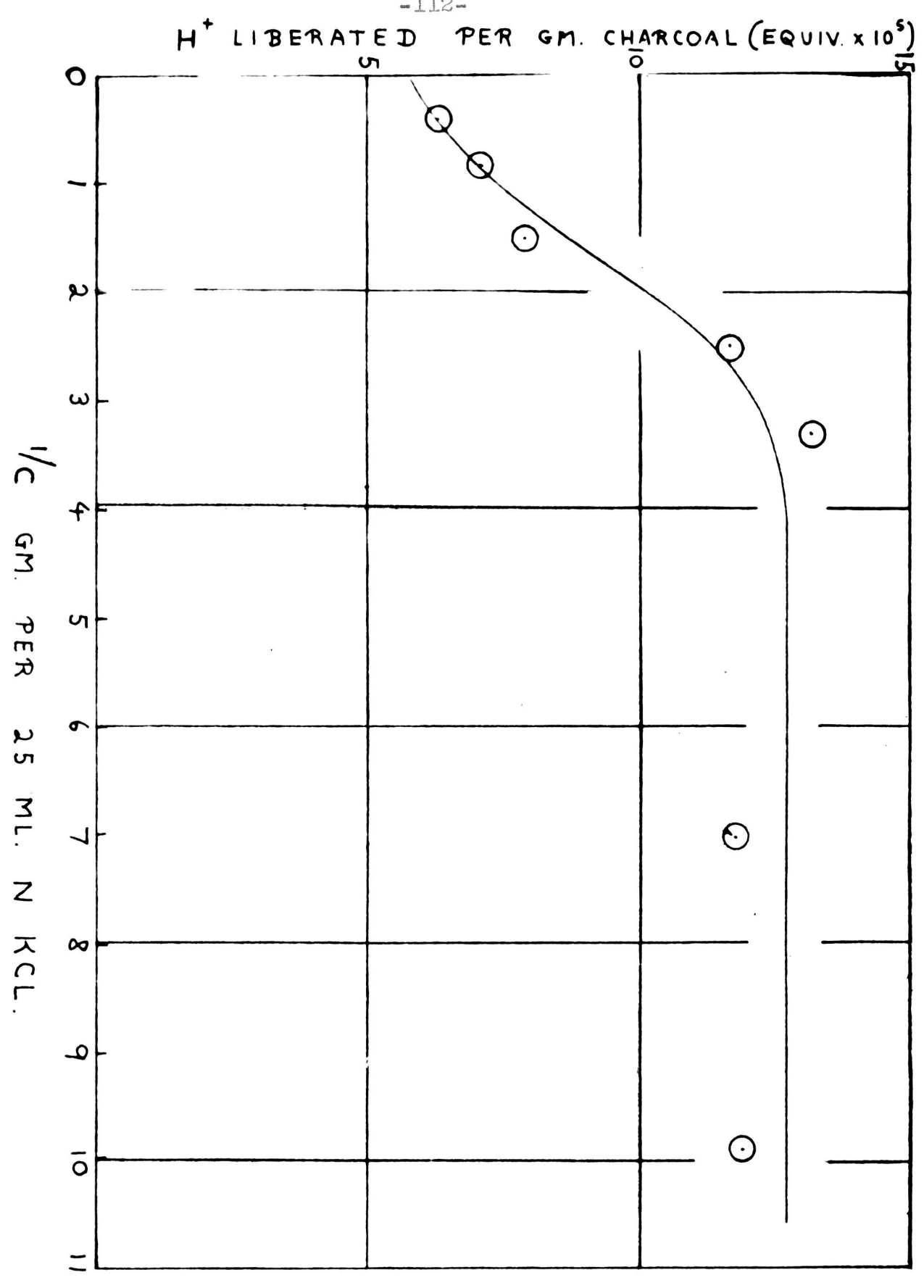
charcoal to the volume of solution varied. The observations are recorded in Table 11 (page 66) and the appropriate derived data are collected in Table 25 (page 111) and graphed in Fig.16.
It is evident that, at constant concentration of neutral salt, increase in volume of the liquid phase of the suspension tended to promote the amount of hydrogen ion liberated, but the maximum value achieved was again not greater than 13 x 10^{-5} equivalents per gm.

The low value might be attributed to the fact that since the base sorbing capacity of the charcoal used was 210 x 10^{-5} equivalents per gm., as compared with 311 x 10^{-5} equivalents for the material used by Wilson and Bolam, there would be sites on the charcoal surface available for adsorbing acid. Thus, the actual amount of liberated hydrogen ion would be greater than 13 x 10^{-5} equivalents, by the amount which had been adsorbed on the appropriate sites. To obtain an estimate of the magnitude of this effect, the adsorption of hydrochloric acid from 0.1N solution by the charcoal used in the above experiments, was determined. It was found to be 4-5 x 10^{-5} equivalents per gm. (Table 16, page 70). Since the highest concentration of acid which could be liberated from the charcoal by the exchange technique would be much less than 0.1N, the adsorption would be less than

Table 25.

Effect of Variation in the Ratio : Volume of Solution/Weight of Charcoal.

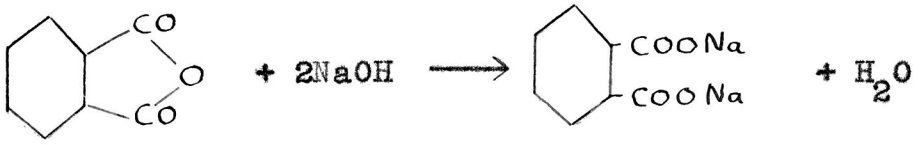
Expt.No.	C=Weight of charcoal per 25 ml. NKCl (gm.)	1/C	H^+ ion liberated per gm. charcoal (10^{-5} equiv.)
1	2.5230	0.40	6.32
2	1.2730	0.79	7.10
3	0.6628	1.50	7.90
4	0.4004	2.50	11.70
5	0.3020	3.31	13.16
6	0.1432	7.00	11.80
7	0.1020	9.80	11.88


H+ LIBERATED PER GM. CHARCOAL (EQUIV. x 10^5)
5
0
15
0
1
2
3
4
5
6
7
8
9
10
11
1/C GM. PER 25 ML. N KCL.

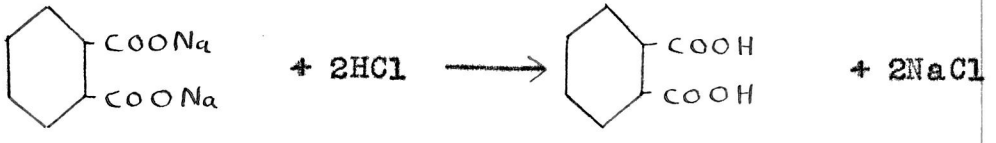
4.5×10^{-5} equivalents. This means that the maximum amount of acid liberated would lie between 13.0×10^{-5} and 17.5×10^{-5} equivalents per gm.

In view of the foregoing considerations, it was concluded that, at most, only 6 - 8 per cent. of the sorption of base could be accounted for in terms of neutralisation of surface carboxyl or phenolic groups.

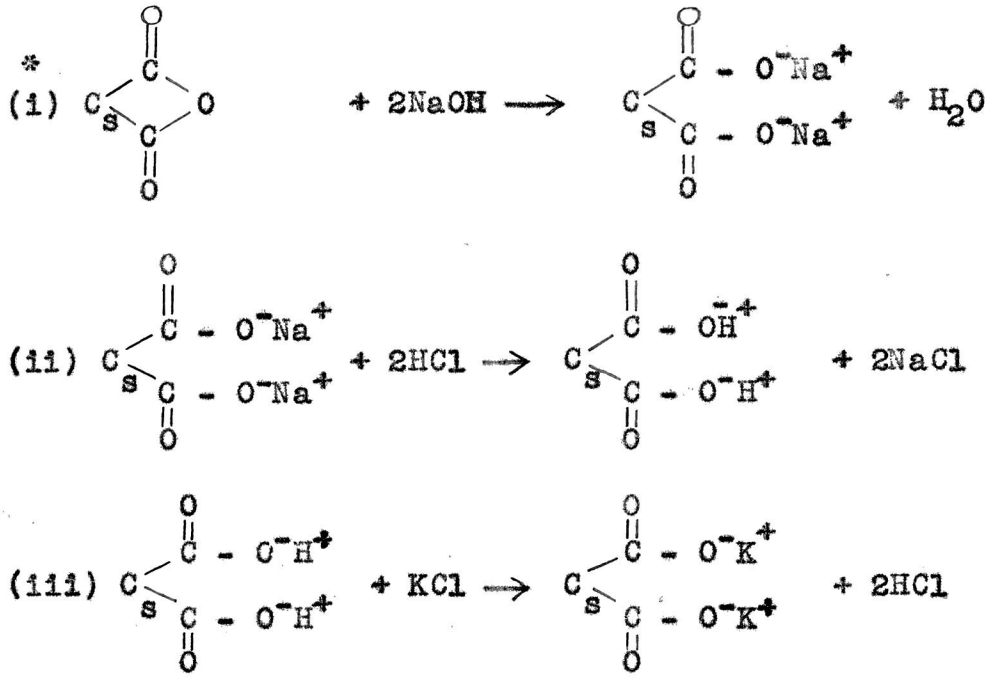
The charcoal was now examined for the presence of some group, capable of reacting with base, yet showing none of the characteristics associated with ion exchange. The anhydride group was envisaged as satisfying such requirements. Anhydrides can be readily hydrolysed at room temperature with dilute alkali, e.g., phthalic anhydride behaves in the following manner:



On acidification, phthalic acid is obtained.



If the oxygen responsible for the sorption of base is present as anhydride groups analogous to phthalic anhydride, the following reactions should take place:



According to the above reaction scheme, the anhydride group reacts with two molecules of base, thus causing the ring system to open. The sodium salt on acidification with hydrochloric acid forms the corresponding acid, which on treatment with neutral salt undergoes ion exchange, thus liberating an amount of acid equivalent to the amount of base sorbed initially. That reaction (ii) might occur, appeared to be indicated by the work of Weller and Young[18], who found that charcoal containing sorbed base, neutralised an approximately equivalent amount of acid.

The surface of the L-charcoal was examined for the presence of anhydride groups in the following manner (see page 67). In brief, a weighed

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* C_s denotes carbon surface.

amount was treated with 25 ml. of 0.2N sodium hydroxide, washed with distilled water and treated with 25 ml. of 0.1N hydrochloric acid. After being washed again, the charcoal was treated with 25 ml. of 1.0N potassium chloride, and the acid content of the filtrate determined.

The data in Table 14 show that, in spite of the above treatment, the liberated acid again amounted to only 13 x 10^{-5} equivalents per gm. Thus it is evident that none of the sorption of sodium hydroxide could be explained in terms of reaction with anhydride groups. The acid liberated after the above treatment could, if due to ion exchange, be accounted for by the following reactions:

$$C_s - COO^-H^+ + NaOH \longrightarrow C_s - COO^-Na^+ + H_2O$$
(or $C_s - O^-H^+$)

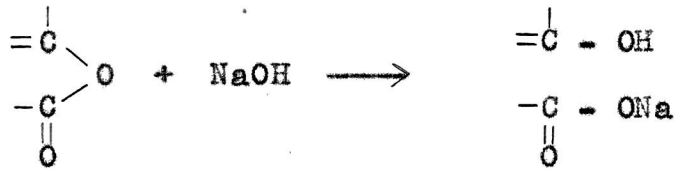
$$C_s - COO^-Na^+ + HCl \longrightarrow C_s - COO^-H^+ + NaCl$$

$$C_s - COO^-H^+ + KCl \longrightarrow C_s - COO^-K^+ + HCl$$

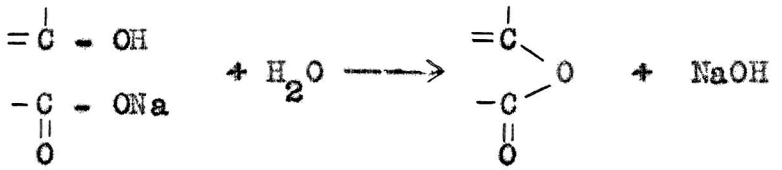
From the data recorded in Tables 12 and 13, it can be seen that though the charcoal sorbed 210 x 10^{-5} equivalents sodium hydroxide per gm., subsequent treatment with 0.1N hydrochloric acid resulted in only 75.3 x 10^{-5} equivalents of acid being adsorbed. The type of organic group which

might explain such behaviour is the lactone group, as may be seen from the following scheme:

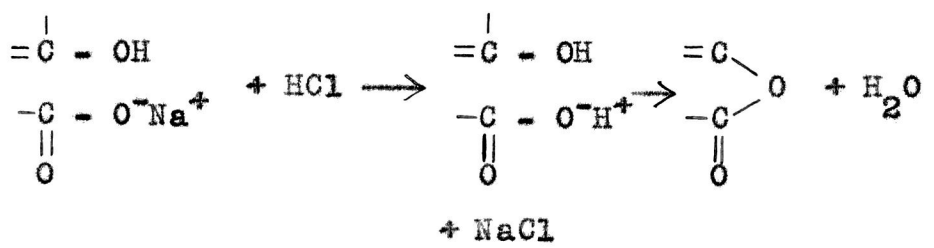
(i) Salt formation, by treatment with sodium hydroxide, to the extent of 197×10^{-5} equivalents (after deduction of 13×10^{-5} equivalents corresponding to acidic hydroxyl or carboxyl groups).



(ii) Hydrolysis of some groups, on washing with water, leading to ring closure, to the extent of $(197 - 75) = 122 \times 10^{-5}$ equivalents



(iii) Ion exchange, in the case of the remaining groups, on treatment with hydrochloric acid, leading to the loss of 75×10^{-5} equivalents of acid, and to ring closure



This scheme would also account for the fact that, in spite of the above treatment, the amount of acid liberated by neutral salt was no greater than in the case of the untreated charcoal. The possibility of the existence of lactone-like complexes on the charcoal surface will be further discussed in connection with the behaviour of the charcoal towards Grignard reagent.

It will be seen from Table 15 that, as a result of the treatment, the sorption of base decreased from 210.5×10^{-5} to 186.5×10^{-5} equivalents. Part (13×10^{-5} equivalents) of this change of 23×10^{-5} equivalents could be due to the displacement of hydrogen ions by exchange with potassium ions as depicted on page 115. The remainder is probably to be ascribed to the loss of finely divided charcoal, by retention in the pores of the sintered-glass disc which supported the charcoal during washing. Comparison of Tables 12 and 15 shows that a loss of charcoal actually occurred. The lost charcoal would possess a relatively high specific surface area and in consequence, a high oxygen, and base sorbing capacity.

Reference to Table 9 shows that even when the charcoal was treated with water only, some acid was liberated, viz. 1.4×10^{-5} equivalents per gm.

This could be due to the desorption of carbon dioxide, or to the extraction of oxalic acid. King[21] detected oxalic acid in charcoals which had been exposed to oxygen and moisture. However, it should be emphasized that despite very thorough washing with water, the sorption of base remained virtually unchanged, indicating that the sorption cannot be due to the action of water-soluble substances present on the surface of the charcoal.

The Action of L-Type Charcoal on Sodium Arsenite.

In the course of his investigation of the influence of the temperature of activation upon the properties of charcoal, King[22] studied what he assumed to be the catalytic activity of the charcoal in respect of the oxidation of a number of easily oxidisable substances. His data were obtained from experiments (at room temperature) in which the charcoal (1 gm.) was suspended in an aqueous solution (50 ml.), of known concentration, of the substance to be oxidised, and oxygen bubbled through the suspension for a short period (30 min.). The solution was then separated from the charcoal and the final concentration of the substance determined in an appropriate volumetric manner. In general, a decrease in concentration was observed, the effect being very small in the case of an H-type charcoal, but markedly greater in that of L-type charcoal.

King attributed the loss of substance to oxidation by the gaseous oxygen, as the result of catalytic action exerted by the "acidic oxide" on the surface of the charcoal. Any such action would, of course, be very much more pronounced with an L-type charcoal than with an H-type charcoal. However, King overlooked the possible operation of two other processes, both of which would produce

loss of reagent. For example, in the case of sodium arsenite, one of the substances examined by him, the arsenite might be (1) adsorbed by the layer of chemisorbed oxygen, or (2) directly oxidised to arsenate by the chemisorbed oxygen. King's data provide no information regarding these possibilities, since he did not determine the amount of oxidation product, or even test for its presence, and no experiments were carried out in which molecular oxygen was excluded from the system.

In the present work, the action of L-type charcoal on sodium arsenite has been re-examined with the main object of ascertaining if the chemisorbed oxygen itself possessed oxidising properties. At the same time the investigation gave an opportunity of establishing if the alleged catalytic activity of the charcoal was a reality, and also of gaining some idea of the extent to which adsorption of the arsenic, as arsenite or arsenate, occurs. Hence the experiments described in Section III of the experimental part were designed to determine the amounts of sodium arsenite and arsenate present (in solution) after treatment, under comparable conditions, of sodium arsenite solutions with (a) gaseous oxygen in the present of L-type charcoal, and (b) L-type charcoal alone.

The precaution was taken of testing, in the first place, for any action of oxygen alone on the arsenite. As will be seen from comparison of the results of Expts. B_1 and B_2 with those of Expts. A_1 and A_2, in the last column of Table 17 (page 84) no change in arsenite concentration occurred when the solution was treated with oxygen in the appropriate fashion. If, however, L-type charcoal was also present, the content of arsenic in the form of arsenite decreased considerably, as is revealed by comparing the data for Expts. C_1 and C_2 with those for Expts. A_1 and A_2 (or B_1 and B_2).

The next step was to estimate what proportion of the decrease in arsenite was due to conversion into arsenate by the treatment with charcoal and oxygen. After titration with bromate, the whole of the arsenic present in the solution would be in the form of arsenate and could therefore be determined by precipitation with uranyl acetate. The difference between the total arsenic and the arsenic present as arsenite after the treatment with charcoal and oxygen, gave the amount of arsenate present in the solution as the result of that treatment. From Table 18 (page 86) it will be seen that the average value of the total arsenic found in Expts. C_1 and C_2 was 0.03448 gm. per 10 ml. solution. Since the average value of the

arsenic as arsenite, in the case of Expts. C_1 and C_2, was 0.03053 gm. per 10 ml., it follows that, on the average, 0.0040 gm. of arsenite had been oxidised to arsenate. Examination of the data for the individual experiments shows that the figure is uncertain by not more than $\pm$0.0007 gm. Thus, though small, the change is real, and proves definitely that oxidation did take place.

The results of Expts. D_1 and D_2 (Table 17) show that when measures were taken to exclude oxygen other than that chemisorbed on the charcoal, the loss of arsenite, and therefore the extent of oxidation, were virtually the same as when oxygen was present (cf. Expts. C_1 and C_2). It must therefore be concluded that the chemisorbed oxygen is capable of direct oxidation of sodium arsenite, and further, that oxidation by molecular oxygen as the result of catalytic action of the chemisorbed oxygen layer, as postulated by King, does not occur.

From the data in Table 18 it appears that the total arsenic decreased considerably, as the result of treatment with charcoal, which can only mean that adsorption of arsenite and/or arsenate took place. The loss of arsenic from this cause was actually 0.03771 - 0.03448 = 0.00323 gm. per 10 ml. solution in the case of 0.0506 molar arsenite, i.e., approximately the same as the loss by

oxidation (0.0040 gm.).

Since the conditions in King's experiments were comparable with those employed in the present work, and since he found that the loss of arsenite in the case of an H-type charcoal was practically negligible compared with L-type charcoal, it follows that the adsorption must take place on the chemisorbed oxygen layer.

It was thought worthwhile to include some determinations at a much higher concentration of arsenite, actually 0.3864 molar. The results (see Table 17, Expts. E_1 and E_2 and F_1 and F_2) indicate a loss of arsenite of 0.2890 - 0.1799 = 0.1091 gm. per 10 ml., thus implying a remarkably high degree of adsorption or oxidation.

It was observed that after treatment with arsenite, the charcoal sorbed less sodium hydroxide than initially, and further, that the decrease was independent of the concentration of arsenite, the uptake of base falling from 210 to ca 177 x 10^{-5} equivalents NaOH per gm. in Expts. C_1, C_2, D_1, D_2, F_1 and F_2. At present, it is not possible to offer any reasonable detailed interpretation of these results, but presumably part of the decrease is due to the removal of chemisorbed oxygen from the surface of the charcoal through interaction with the arsenite. The matter seems to be worthy of further study.

Finally, it became clear from the results of this portion of the work that oxidation processes might play an important part in the interaction of L-type charcoal with Grignard reagent, at the much higher temperature of 181°.

Interaction Between Charcoal and Grignard Reagent.

The preliminary work on the investigation of the interaction of charcoal with Grignard reagent was carried out using Preparation I. When the data for L- and H-type charcoals are compared (Expts.1a and 1b, Table 20), it will be seen that the volume of gas evolved on heating at 181° for 2 hours was greater in the case of the L-charcoal, viz., 19.08 ml. as compared with 12.78 ml. for the H-material. On increasing the time of reaction to 5 hours (Expts.2a and 2b), the volume of gas evolved during the first stage was greater for both types of charcoal, viz., 26.35 ml. and 14.99 ml. respectively. The concentration of Grignard reagent, in the case of the L-type charcoal, had fallen after 5 hours to a negligible value. Hence, in order to furnish conditions suitable for ascertaining at what point the reaction between L-charcoal and Grignard reagent would be complete, it was necessary to increase the concentration of the reagent.

To this end, the conditions of preparation of the reagent were altered, in that the final addition of di-isoamyl ether was omitted. This resulted in much of the reagent appearing in permanently colloidal form, but the concentration was seven to ten times greater than that of Preparation I. However, in the experiments (3a and 3b) with the new preparation (Preparation II), the volume of gas proved to be less than that in the corresponding experiments with Preparation I. It seemed probable that the pores of the charcoal were blocked by colloidal particles of the reagent, so that a large part of the charcoal surface was not accessible to the reagent.

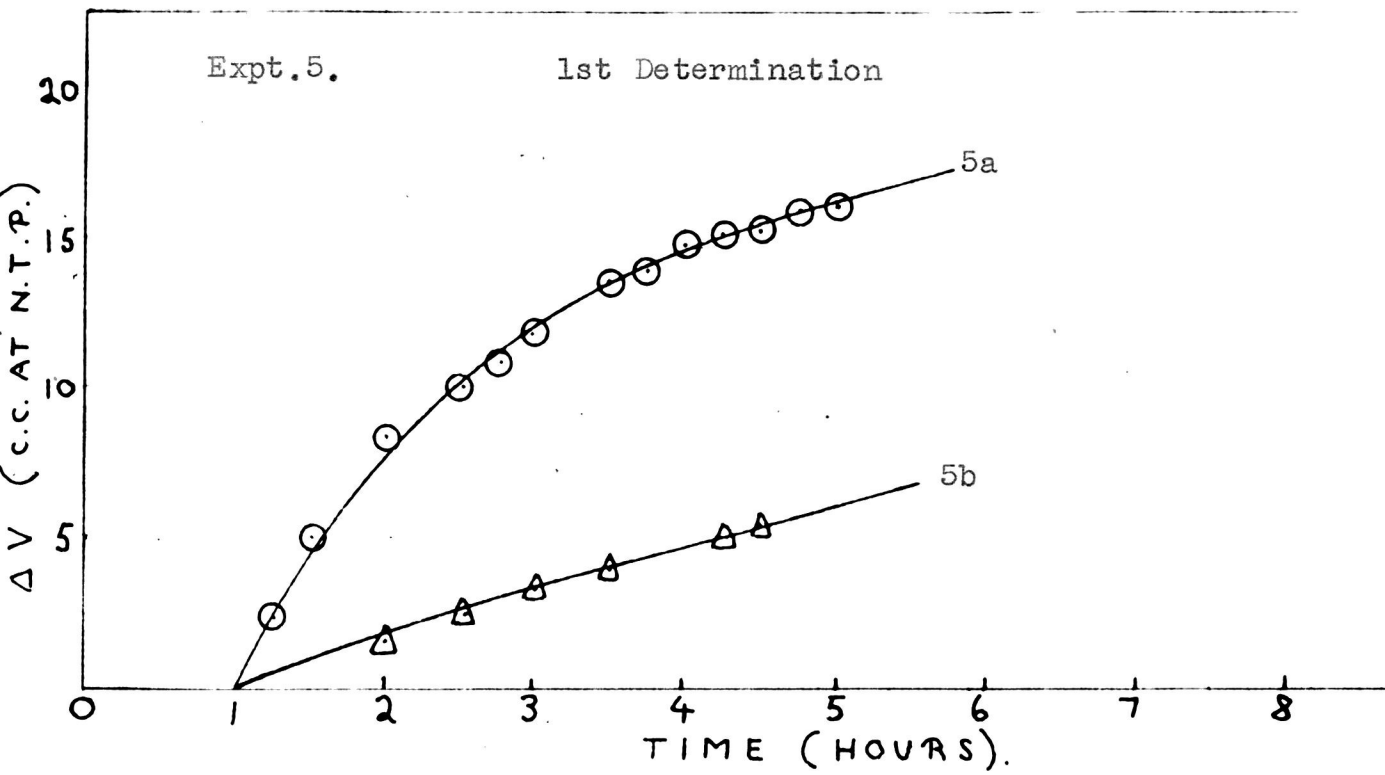
With Preparations III and IV, where the concentration of reagent was intermediate between those of Preparations I and II, satisfactory conditions for studying the interaction between charcoal and Grignard reagent were obtained. As stated on page 89, in the case of Preparation III, 100 ml. of di-isoamyl ether were added in the final step of the preparation. It was found that this represented the minimum amount of ether which could be added without the methyl magnesium iodide appearing in a permanently colloidal form. The suspended solid which was present in Preparation III eventually settled out, and the supernatant liquid could be decanted. This solution could be

considered saturated with respect to methyl magnesium iodide, and therefore represented the maximum concentration of Grignard reagent which could be obtained under the conditions of preparation used. 10 Ml. of this solution, when treated with excess of water gave 65.66 ml. of methane, and subsequent preparations of the reagent were designed to give approximately this concentration.

The use of Preparation III, as will be seen from Expts. 4 and 5, produced a large increase in the volume of gas evolved in the first stage, as the result of the increase in effective concentration of the reagent (cf. Preparation I). In Expts. 5a and 5b, the rate of evolution of gas was measured during the last four hours of heating, and the data (Table 21, page 101 and Fig.17) showed that in the case of the L-type charcoal (Expt. 5a), the rate probably became constant after about four hours. Confirmation was obtained by extending the period of heating to seven hours (Expt.7a, Table 21 and Fig.18). As is evident from the curves of Expts.5b and 7b, in the case of the H-type charcoal constancy of rate was attained after roughly 1.5 hours.

Comparison of corresponding curves in Figs.17 and 18 show that satisfactory reproducibility of the rate curves was achieved, although

Fig.17.


Expt.5.
1st Determination
5a
5b
ΔV (C.C. AT N.T.P.)
TIME (HOURS).

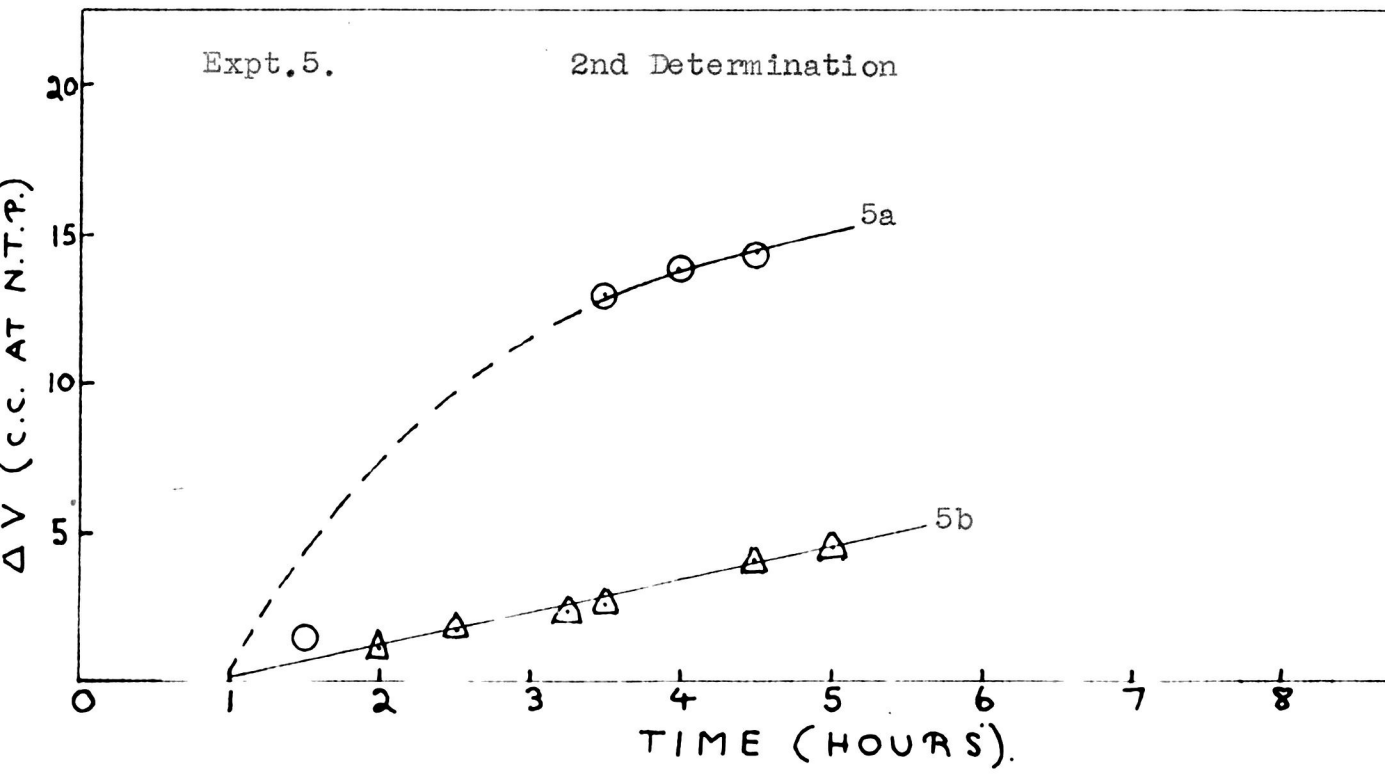
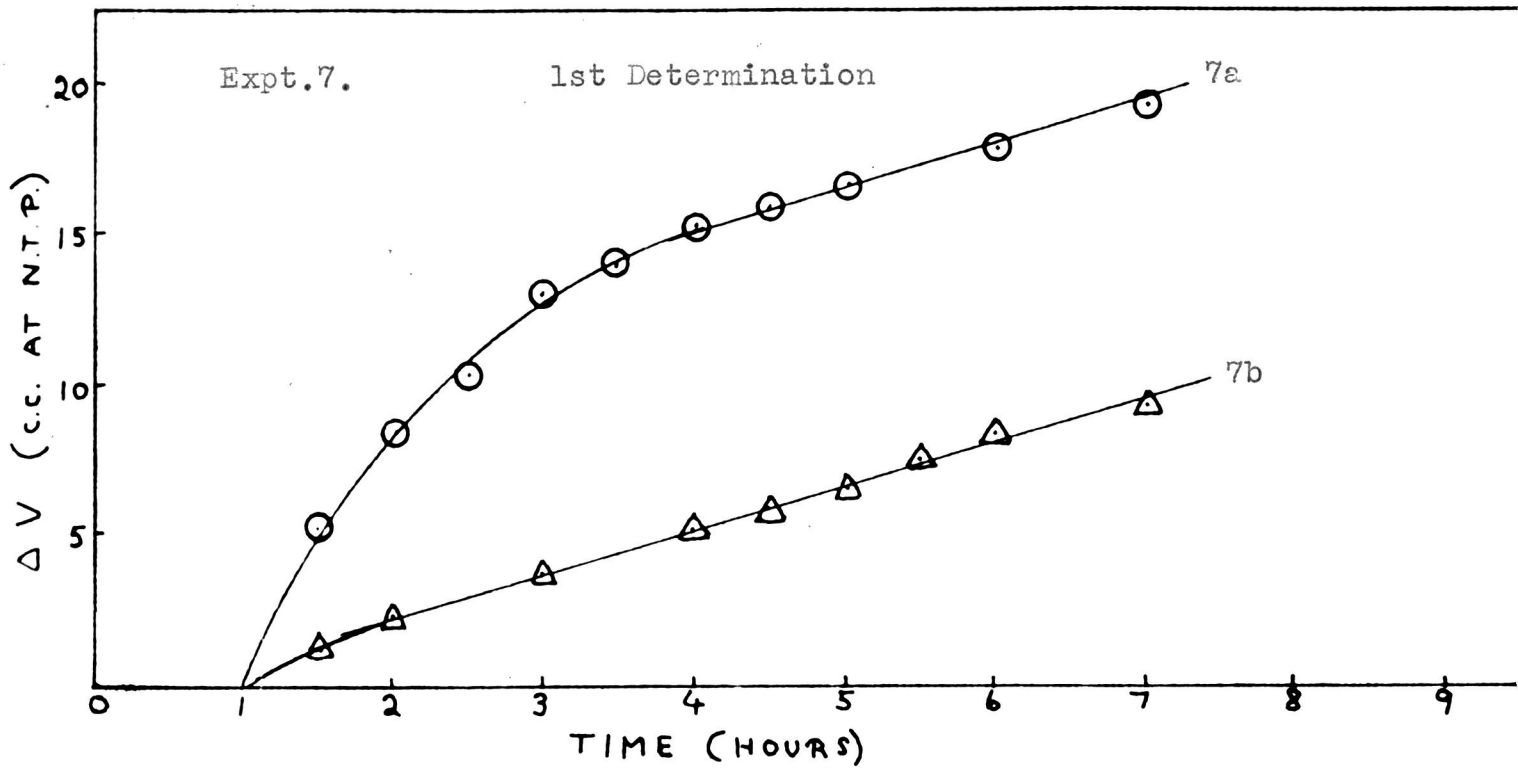
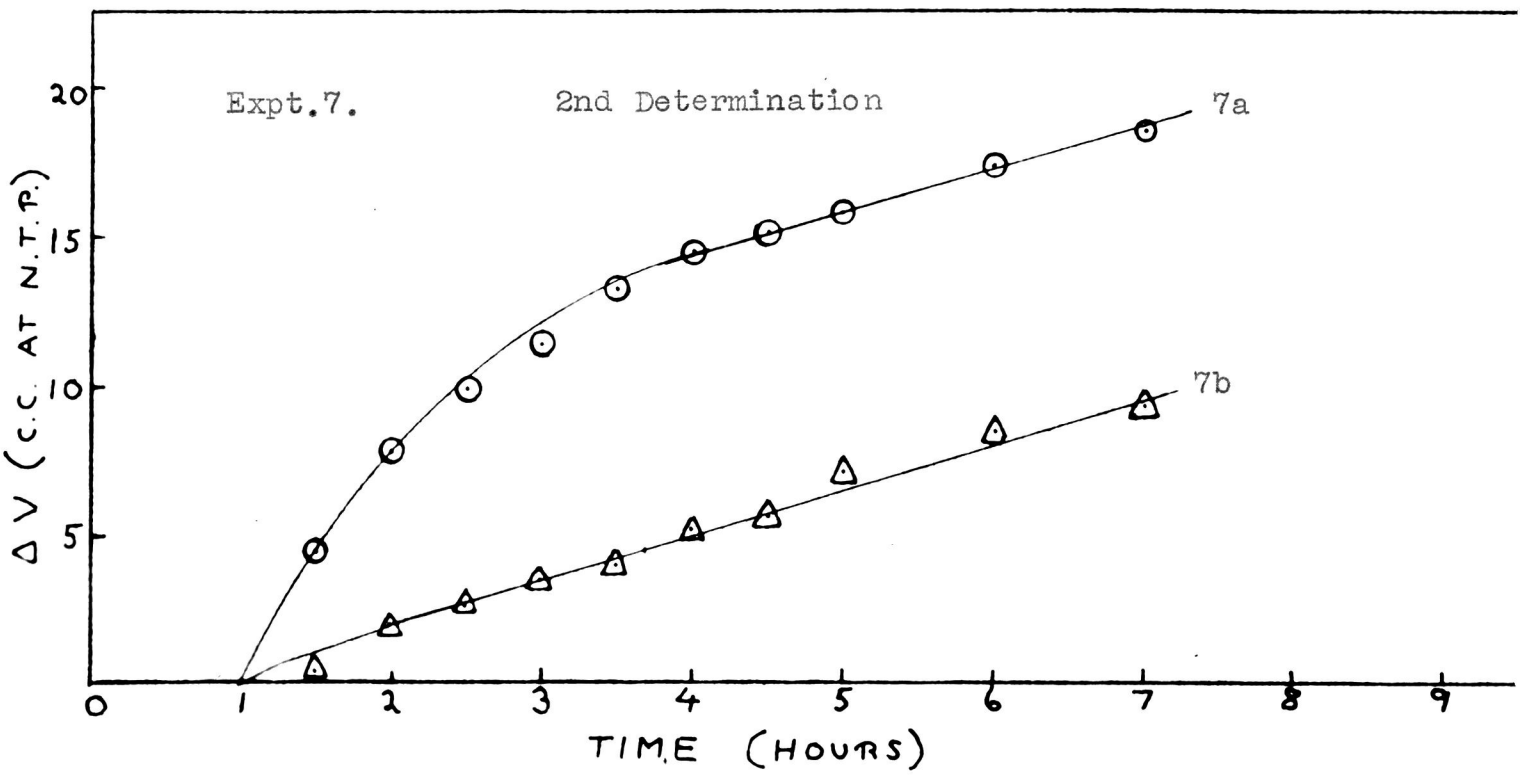

Expt.5.
2nd Determination
5a
5b
ΔV (C.C. AT N.T.P.)
TIME (HOURS).

Fig.18.


Expt.7.
1st Determination
7a
7b
ΔV (c.c. AT N.T.P.)
20
15
10
5
0
1
2
3
4
5
6
7
8
9
TIME (HOURS)


Expt.7.
2nd Determination
7a
7b
ΔV (c.c. AT N.T.P.)
20
15
10
5
0
1
2
3
4
5
6
7
8
9
TIME (HOURS)

different preparations of reagent (of the same concentration) were used in Expts. 5 and 7. Accordingly, the observed rates have quantitative significance. The salient feature is, that the final rate obtained with L-charcoal was identical with the rate given by H-charcoal during most of the period of thermal treatment. In other words, the difference in volume of gas evolved in the two cases ultimately became constant (at four hours), showing that the reaction which produced the initial difference in rate had ceased. Two reactions appear to be involved. One proceeds at the same rate, irrespective of the type of charcoal, and continues as long as the concentration of the reagent is kept sufficiently high. The other depends upon the amount of oxygen present on the charcoal surface, terminating in about four hours in the case of L-charcoal and in a much shorter period in that of the H-charcoal.

This view is supported by the results of analysis of the gas evolved in 7 hours. The appropriate data are collected in Table 24 (page 106), and show that the gas from both L- and H-charcoal experiments had the same composition, comprising only methane, ethane and nitrogen. Moreover, quantitative analysis revealed that although the percentage of methane was greater in the case of L-charcoal, the ethane percentage remained the

same. Since no other gas appeared to be present as the result of the reaction, the difference in the total volume of gas evolved during the first stage of the reaction with L-charcoal on the one hand, and H-charcoal on the other, appears to consist solely of methane. Confirmation is provided by the data recorded in Table 26 (page 131), in which V_L and V_H represent the total volumes of gas evolved in the first stages of the L- and H-charcoal experiments respectively, and V_L^1 and V_H^1 the volumes obtained during the corresponding second stages. It will be seen that the differences $(V_L - V_H)$ and $(V_L^1 - V_H^1)$ are equal, irrespective of the time of reaction of the first stage or the concentration of Grignard reagent used. This equivalence can only be interpreted by supposing that the difference $(V_L - V_H)$ is due entirely to methane, and that loss of reagent in any form other than methane occurred to the same extent in the case of both L- and H-charcoal.

Since the chief difference between L- and H-charcoals is the presence of the chemisorbed layer of oxygen on the former, it is reasonable to suppose that the preponderance of methane present in the gas from the L-charcoal experiments, is, in some manner, associated with this oxygen.

Table 26.

Comparison of L-charcoal with H-charcoal.

1st Stage					2nd Stage				
L-charcoal		H-charcoal		Difference	L-charcoal		H-charcoal		Difference
Expt.	V_L	Expt.	V_H	$V_L - V_H$	Expt.	V_L^1	Expt.	V_H^1	$V_H^1 - V_L^1$
1a	19.08	1b	12.78	6.30	1a	14.16	1b	19.47	5.31
2a	26.35	2b	14.99	11.36	2a	1.21	2b	11.89	10.68
3a	12.01	3b	10.50	1.51	3a	75.59	3b	77.02	1.43
4a	22.22	4b	17.66	4.56	4a	42.36	4b	46.76	4.40
5a	37.29	5b	21.49	15.80	5a	15.96	5b	31.98	16.02
6a	22.75	6b	18.20	4.55	6a	33.47	6b	36.28	2.81
7a	41.59	7b	25.94	15.65	7a	13.50	7b	28.77	15.27

The interaction of Grignard reagent and L-charcoal could conceivably give rise to methane in a number of ways. It is well known that L-charcoal is much more hygroscopic than H-charcoal, and it might be supposed that the methane arises from interaction between the Grignard reagent and water adsorbed on the charcoal surface. However, the charcoal was heated in vacuum for one hour at 181° prior to the addition of the reagent (see page 95) and the possibility of any water remaining on the surface after this treatment seems very unlikely. The possibility of the production of methane by interaction of reagent with hydroxyl groups on the surface of the charcoal must be taken into consideration, since there is evidence[1] that the charcoal would contain hydrogen in some form other than physically adsorbed water. It is not unreasonable to suppose that hydroxyl groups might be formed by reaction between this hydrogen and the oxygen employed for the activation at 400°.

In Table 23, the data for the sorption of base by charcoals L_3 and L_4, after treatment with Grignard reagent, are recorded. The charcoals could initially sorb 210 and 187 x 10^{-5} equivalents sodium hydroxide per gm., and, by reference to Table 27, it will be seen that in every case a reduction in sorption had occurred. This reduction is

consistent with the view that acidic hydroxyl groups are present, since these would undergo reaction with Grignard reagent in the following manner

$$C_5 - COOH \text{ (or } C_5 - OH) + CH_3MgI \longrightarrow C_5 - COOMgI + CH_4$$

Thus after treatment the sorption will be less than originally, because some of the functional groups have reacted with the reagent.

However, in view of the fact that few acidic hydroxyl groups could be detected by ion-exchange measurements, and of the evidence of the direct oxidation of arsenite to arsenate by chemisorbed oxygen, it seems more satisfactory to ascribe the reduction in base-sorbing capacity to removal of oxygen from the chemisorbed layer. In support of this view, it is highly significant that the sorption decreased when the charcoal was heated with di-isoamyl ether alone (Table 23). Moreover, from Table 27 it will be seen that the amount of decrease was the same, irrespective of whether the charcoal was heated with Grignard reagent or with di-isoamyl ether alone. The simplest explanation appears to be that the ether was oxidised by the chemisorbed oxygen, and the capacity of the charcoal to sorb base thereby reduced.

However, any mechanism proposed must take

Table 27.

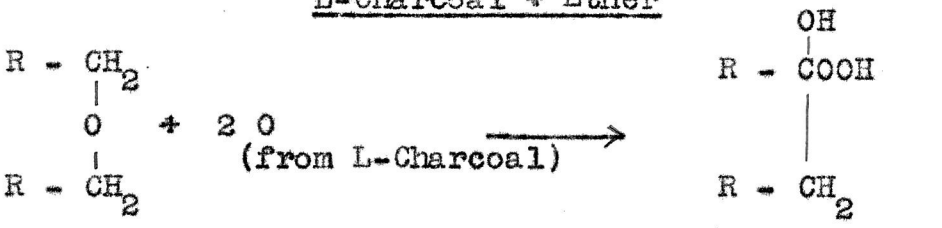
Correlation of Sorption of Base with Production of Methane.

Period of heating at 181° (hours)	Expt. No.	System	Decrease in sorption of NaOH per gm. charcoal (10^{-5}equiv.)	Volume of gas evolved per 0.5 gm. charcoal (c.c.at N.T.P.) From graph	Loss of oxygen per gm. charcoal (10^{-5}gm.atom.)	Loss of oxygen / Decrease in NaOH sorptn. Gm.atoms. / Moles
2	4a	L_3+G.R.*	210-120= 90	30.6	352	3.9
	6a	L_4+G.R.	189-101= 88	30.6	352	4.0
	-	L_4+Ether	189- 96= 93	-	-	-
5	5a	L_3+G.R.	210- 83=127	38.9	407	3.2
	-	L_4+Ether	189- 64=125	-	-	-
7	7a	L_3+G.R.	210- 76=134	41.6	444	3.3

*G.R. = Grignard reagent.

into account the production of methane in the reaction with Grignard reagent, for it will be noticed that the decrease in sorption became constant after the production of methane had ceased, having approximately the same value for periods of reaction of five and seven hours. It seems possible that the evolution of methane, and the identity in the reduction of sorption of base by Grignard reagent and di-isoamyl ether, may be explained by the following mechanisms.

L-Charcoal + Ether

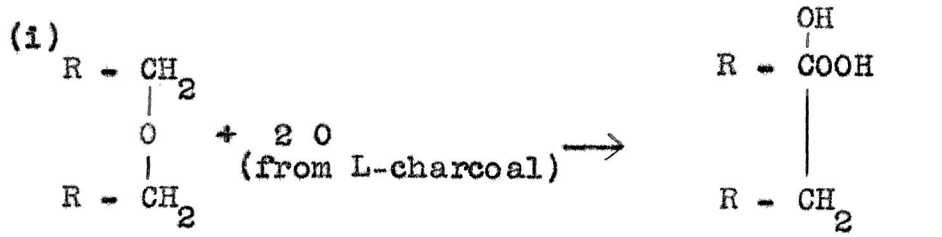


di-isoamyl ether — hydroperoxide

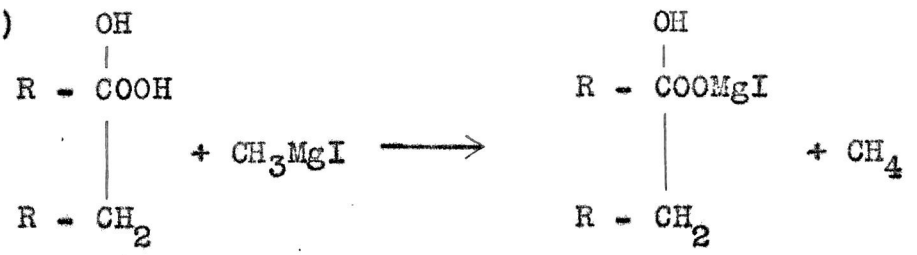
i.e., one molecule of the ether reacts with two oxygen atoms from the charcoal to produce one molecule of hydroperoxide. Thus, for every molecule of the hydroperoxide formed, the sorption of base decreases by an amount equivalent to the loss of two atoms of oxygen.

L-charcoal + Grignard reagent

(i)



di-isoamyl ether — hydroperoxide

(ii)


i.e., the first step is the same as the reaction with ether alone, and therefore the reduction in sorption will be the same. In addition, each molecule of the hydroperoxide formed will react with one molecule of methyl magnesium iodide to form an equivalent amount of methane. Thus, for every molecule of methane formed, the sorption should decrease by an amount equivalent to the loss of two atoms of oxygen.

According to the foregoing scheme, theoretically, all the chemisorbed oxygen capable of sorbing base should be capable of reacting with the ether, and, provided the concentration of the ether is kept sufficiently high, the reaction should proceed until the sorption has been reduced to zero. This however did not happen, since the reduction in base sorption became constant after about five hours. It is probable that, while (according to the work of Bolam and Wilson[1]) almost all, if not all, of the oxygen is accessible to sodium hydroxide, a proportion of it will be situated in very fine pores into which the ether molecules, because of their size, cannot pass. Obviously the reaction will

proceed only to the extent to which oxygen is accessible to the ether.

From Table 27 it will be seen that, irrespective of the initial amount of sorption (L_3 = 210 x 10^{-5} equiv. per gm.: L_4 = 189 x 10^{-5} equiv. per gm.), reduction in the sorption occurred to approximately the same extent, viz., 90 x 10^{-5} equiv. and 88 x 10^{-5} equiv. respectively in the case of the 2 hour experiments. This would imply that the amount of oxygen accessible to the ether is the same in both charcoals, but that there was more inaccessible oxygen present in L_3 than in L_4. It seems feasible to postulate that owing to a greater degree of activation in the case of the L_4 material, the development of very fine pore-structure had proceeded further.

It will now be shown that on the basis of the mechanism proposed above, it is possible to arrive at values of the ratio

$$\frac{\text{Chemisorbed Oxygen content per gm. charcoal}}{\text{Maximum amount of NaOH sorbed per gm. charcoal}}$$

comparable with those obtained by Weller and Young[18] and by Wilson and Bolam[1], who determined the oxygen content of their charcoals by direct means.

Two of the charcoals studied by Weller and Young (viz. Tuc-45 and Tuc-60) sorbed 220 and 230 x 10^{-5} equivalents sodium hydroxide per gm.

respectively, the total oxygen contents being 12.7 and 13.5 per cent. These percentages correspond to 794 and 844 x 10^{-5} gm. atom of oxygen per gm., and the ratios of oxygen/sodium hydroxide are therefore 3.6 and 3.7.

Wilson and Bolam determined the amount of chemisorbed oxygen, liberated as carbon monoxide and carbon dioxide, on heating their L-charcoals in a stream of nitrogen until the sorption of base (initially 313 x 10^{-5} equivalents per gm.) had been virtually reduced to zero. The amount of oxygen obtained in this way was 165.4 mg. or 1034 x 10^{-5} gm. atom per gm. Hence the ratio was 3.3.

The ratio obtained by Weller and Young is possibly too high, since the figure for total oxygen found by what is described as "ultimate" analysis, may in fact include some physically adsorbed gas. No details regarding the analytical procedure are given.

According to the proposed mechanism for the production of methane, each molecule of methane results from the action of two atoms of oxygen. This relation provides the basis for the following calculation of the oxygen/base ratio from the data obtained in Expt. 7a.

From Table 20

(a) Total volume of gas obtained after heating L-charcoal with Grignard reagent for 7 hours at 181° = 41.6 c.c.

From Table 22

(b) Total volume of gas obtained after heating L-charcoal with ether alone for 5 hours at 181° = 9.4 c.c.

With regard to (b), it will be seen from Table 22 that the volume of gas was virtually constant during the period of heating from 2 to 5 hours. Hence, the volumes obtained by heating at 5 and 7 hours may be regarded as substantially the same, and it appears from analysis that this gas was desorbed nitrogen.

(a) - (b) = 32.2 c.c., which will consist of methane and ethane.

From Table 24

Volume of methane = $\frac{32.2}{1} \times \frac{17.2}{17.2+5.1}$ = 24.8 c.c.

Since 24.8 c.c. of methane were produced by 0.5 gm. charcoal,
then 49.6 c.c. of methane were produced by 1.0 gm. charcoal.

Also 49.6 c.c. ≡ 222×10^{-5} mole methane.

∴ Corresponding amount of chemisorbed oxygen
= 444×10^{-5} gm. atom.

From Table 27

Decrease in sorption of sodium hydroxide per gm. charcoal = 134×10^{-5} equiv. per gm.

$$\therefore \frac{\text{Amount of chemisorbed oxygen}}{\text{Decrease in sorption of NaOH}} = \frac{444}{134} = 3.3$$

The agreement with the value of the ratio obtained by Wilson and Bolam affords good support for the proposed mechanism. The identity of values however, must be considered coincidental, as the value calculated above is obviously subject to several per cent. error.

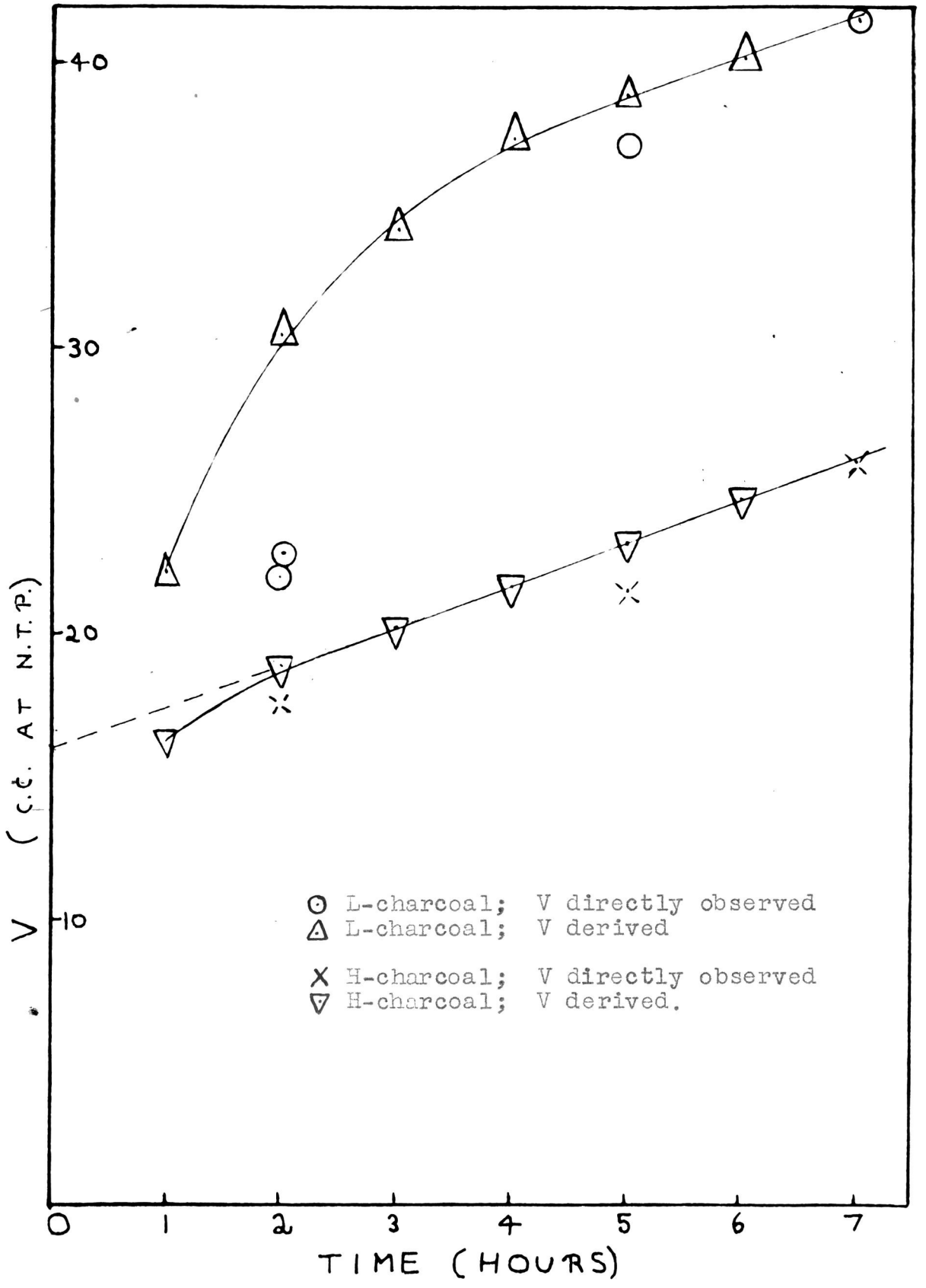
Fig.19 shows the variation of the total volume (V) of gas evolved at 181°, with the period of heating. The curves are drawn through points for which V was derived from the upper curve of Fig.18 (Expt. 7, 1st determination) in the following way. At 7 hours the value of V found directly was 41.6 c.c. (Table 20), while that of Δ V was 19.4 c.c. (Table 21). Hence to obtain the points for the V curves, the difference, 41.6 - 19.4 = 22.2 c.c., was added to the corresponding values of Δ V. It is evident that the values of V found directly lie close to the curves, except for the value for L-charcoal at 2 hours.

There can be no doubt that the discrepancy at 2 hours is anomalous, because the degree of reproducibility of the experiments excluded an error of such magnitude. It would seem that there was resorption of some of the gas on cooling the system when the reaction was terminated after 2 hours, and

that this gas was again expelled when the system was treated with water in the second stage of the procedure. The reason this did not occur with longer periods of heating may be connected with the circumstances that at 2 hours, the evolution of methane was still proceeding vigorously and the pores of the charcoal were full of gas, whereas at 5 and 7 hours, all the gas would have been expelled and the pores filled with liquid.

The curves in Fig.19 may be used to calculate values of the oxygen/base ratio for the intervals of 2 and 5 hours, if it be assumed that the gas produced in the reaction of constant rate was ethane. On this assumption, the volume of ethane produced in 7 hours may be deduced as follows. Extrapolation of the linear portion of the lower curve in Fig.19 cuts the y-axis at 16.5 c.c. Making the reasonable further assumption that no appreciable formation of ethane occurred before the temperature attained 181°, it is evident that the volume of ethane evolved in 7 hours would be 25.9 c.c. (total gas produced in 7 hours) - 16.5 = 9.4 c.c. The actual volume of ethane found in the case of the L-charcoal was, according to the calculation on page 139, 32.2 - 24.8 = 7.4 c.c. A similar calculation for the H-charcoal (Expt. 7b) gave 9.0 c.c. The substantial agreement between the three values

Fig.19.


40
30
20
10
V (c.c. AT N.T.P.)
0
1
2
3
4
5
6
7
TIME (HOURS)
L-charcoal; V directly observed
L-charcoal; V derived
H-charcoal; V directly observed
H-charcoal; V derived.

strongly suggests that the gas produced in the slow reaction was ethane.

The values of the oxygen/base ratio obtained by adopting this point of view are shown in the last column of Table 27 (page 134). They were calculated from the data for Expts. 4, 5 and 6, in the manner illustrated on page 139, except that the volume of methane was derived from the relation

Total volume of gas evolved with L-charcoal - volume of desorbed nitrogen - (total volume of gas evolved with H-charcoal - 16.5 c.c.).

It is evident that in all cases the ratio lies between 3.0 and 4.0, the value being nearer 3 for the longer period of heating. This resemblance to the values of the ratio obtained by Wilson and Bolam (3.3) and Weller and Young (3.6) affords further support for the mechanism proposed for the production of methane.

Wilson and Bolam postulate that two types of oxygen "complex", α and β, are involved in the sorption of base, the ratio of atoms of oxygen to molecules of base being 2:1 in the case of α and 4:1 in the case of β. Accordingly, in a given instance, the ratio obtained would depend on the relative proportions of the complexes affected during the prescribed period of heating with Grignard reagent.

Since it would appear that the production of methane is due to interaction between the chemisorbed oxygen and di-isoamyl ether to give hydroperoxide, it seems reasonable to suppose that the oxygen is attached to the carbon surface in such a manner that two oxygen atoms remain united, that is to say, the most probable structures are

On this view, the sorption of base cannot be attributed to the reaction of lactone groups present on the surface of the charcoal (see page 117).

In conclusion it may be pointed out that the production of ethane appears to arise from thermal decomposition of the Grignard reagent, since the amount formed, under comparable conditions, is independent of the type of charcoal used. The results of the few experiments in which the reagent was heated at 181° in the absence of charcoal are given in Table 19 (page 98). They show that decomposition to give gaseous products occurred, but the data are not sufficiently extensive to yield any further information.

Sorption of Base by L-Type Charcoal from Aqueous-Alcoholic Solution.

Hoffmann and Oberliche[23] found that Carboraffin coke, prepared at 1000° in hydrogen, nitrogen or vacuum, and treated with a mixture of concentrated sulphuric and nitric acid at 800°, sorbed different amounts of base from aqueous and alcoholic solutions. Prior to the sorption experiments the charcoal was washed until no appreciable amount of sulphur or nitrogen remained in the material. The sorption was determined by placing 0.1 gm. of charcoal in 50 ml. of 0.05N alkali for 12 hours. It is recorded that 400 x 10^{-5} equiv. sodium hydroxide per gm. were sorbed from aqueous solution. With alcoholic potassium hydroxide, the uptake was 750 x 10^{-5} equiv. The above workers suggested that perhaps two types of hydroxyl groups were present. The one (= 350 x 10^{-5} equiv.) was weakly acidic and was neutralised only by alcoholic base, its potassium salt being hydrolysed by water. The other (= 400 x 10^{-5} equiv.) was strongly acidic, and could be neutralised with aqueous as well as alcoholic base.

In the course of the present work, experiments were carried out to ascertain if the effects reported by Hoffmann and Oberliche were obtainable with L-type sugar charcoal. The sorption of

potassium hydroxide from 0.05N aqueous-alcoholic solution (about 98 per cent. alcohol), and, for comparison, that from 0.05N aqueous sodium hydroxide was determined by the usual procedure, the charcoal from batch L_2 being used. This was the only occasion on which the normality of the base differed from 0.2N. The data recorded in Tables 28 and 29 show, beyond doubt, that the presence of alcohol had no effect upon the sorption of the base, in accordance with the findings of Steenberg (see page 8).

Physical Adsorption of Base.

The present investigation has shown that, at the best, only a small fraction of the sorption of base by L-charcoal can be accounted for in terms of chemical reaction with well-recognised groups present on the carbon surface. Hence, it would appear that serious consideration should be given to the possibility that the base may be physically adsorbed on the layer of chemisorbed oxygen. In this connection it may be significant that Wilson[24] found that the hydroxides of the alkali metals are not equally strongly sorbed under comparable conditions, the soquence being LiOH > NaOH > KOH. It is difficult to explain these differences in behaviour on chemical grounds. On the other hand,

it is not easy to see how a theory of physical adsorption could account for the existence of two types of sites, on the oxygen layer, corresponding to the α - and β -complexes postulated by Bolam and Wilson[1].

Oxidation of Charcoal by Hydrogen Peroxide.

King[22] examined a series of charcoals which had been activated at temperatures within the range 240° - 1130°, from the standpoint of their activity in decomposing hydrogen peroxide, and found that the degree of decomposition depended to a marked extent upon the temperature at which the charcoal had been activated. He showed that minimum activity was exhibited by L-charcoals activated at about 400° and maximum activity by H-charcoals activated at about 920°. It appeared that the rate of oxygen evolution from a suspension of H-charcoal in hydrogen peroxide solution was initially high, but fell rapidly until after about two hours, a low constant rate was reached. King referred to the initial phase of rapid evolution of gas as α - activity, and the slow constant evolution as β - activity. The rate of oxygen evolution in the case of an L-charcoal was virtually always low and constant, and corresponded to the β -activity exhibited by an H-charcoal after two hours.

Table 28.

Sorption from Aqueous-Alcoholic KOH Solution by L-Type Charcoal.

Weight of charcoal (gm.)	Change in titre on 10 ml. 0.05N KOH (ml. 0.1N HCl)	Equivalents KOH sorbed per gm. charcoal (x 10^5)
0.3030	1.91	157.8
0.3020	1.89	154.0

Table 29.

Sorption from Aqueous NaOH Solution by L-Type Charcoal.

Weight of charcoal (gm.)	Change in titre on 10 ml. 0.05N NaOH (ml. 0.1N HCl)	Equivalents NaOH sorbed per gm. charcoal (x 10^5)
0.3020	1.90	154.0
0.3010	1.88	153.6

In Curve I of Fig.20 the data for the duplicate runs 14 and 15 (Table 6, page 53) are graphed. In these experiments the conditions used by King in obtaining his data for an H-charcoal were simulated, but the oxygen evolution rate curve, in marked contrast to that obtained by him (reproduced in Fig.20, Curve II), shows no sharp break after 50 minutes, corresponding to the change from α - to β -activity.

The hydrogen peroxide used in runs 14 and 15 contained no inhibitor (King does not state whether or not the material he used contained inhibitor), but it appears from the present work that the presence of inhibitor has no effect upon the general shape of the decomposition curve. This is shown by Curve I of Fig.21, in which the data of run 3 are plotted, and the minimum and maximum volumes of oxygen evolved in the same time intervals in runs 1, 2, and 4 to 9 are indicated by vertical lines. The peroxide used in runs 3 to 9 contained inhibitor, while that in the other runs was free from it. Nevertheless, the volume of oxygen evolved after a given time interval was substantially the same in all cases.

The rate of oxygen evolution was also independent of the method of agitation of the suspension. In runs 6 and 7 the contents of the reaction vessel

Fig.20.

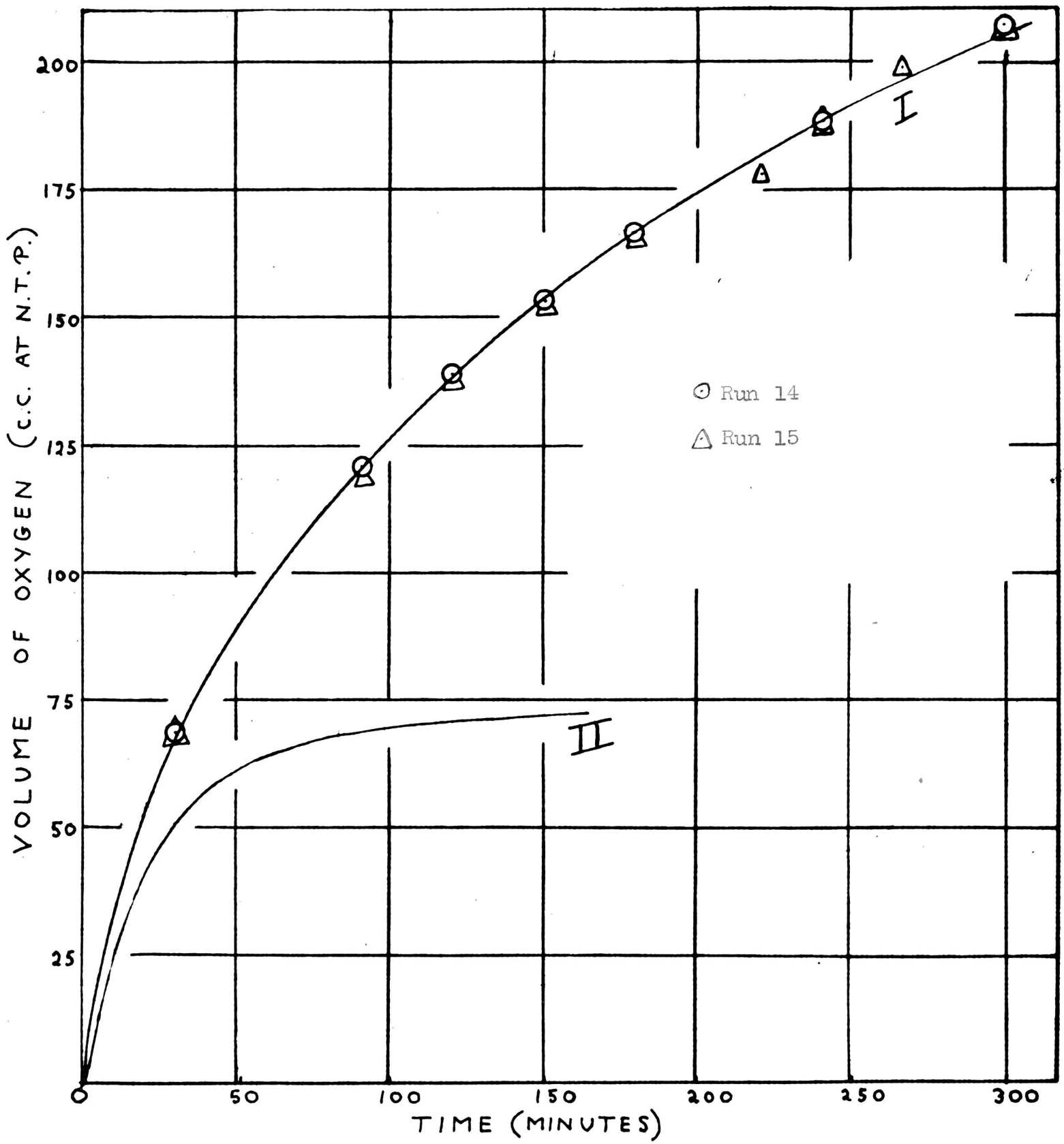

200
175
150
125
100
75
50
25
VOLUME OF OXYGEN (C.C. AT N.T.P.)
0
50
100
150
200
250
300
TIME (MINUTES)
I
II
Run 14
Run 15

Fig.21.

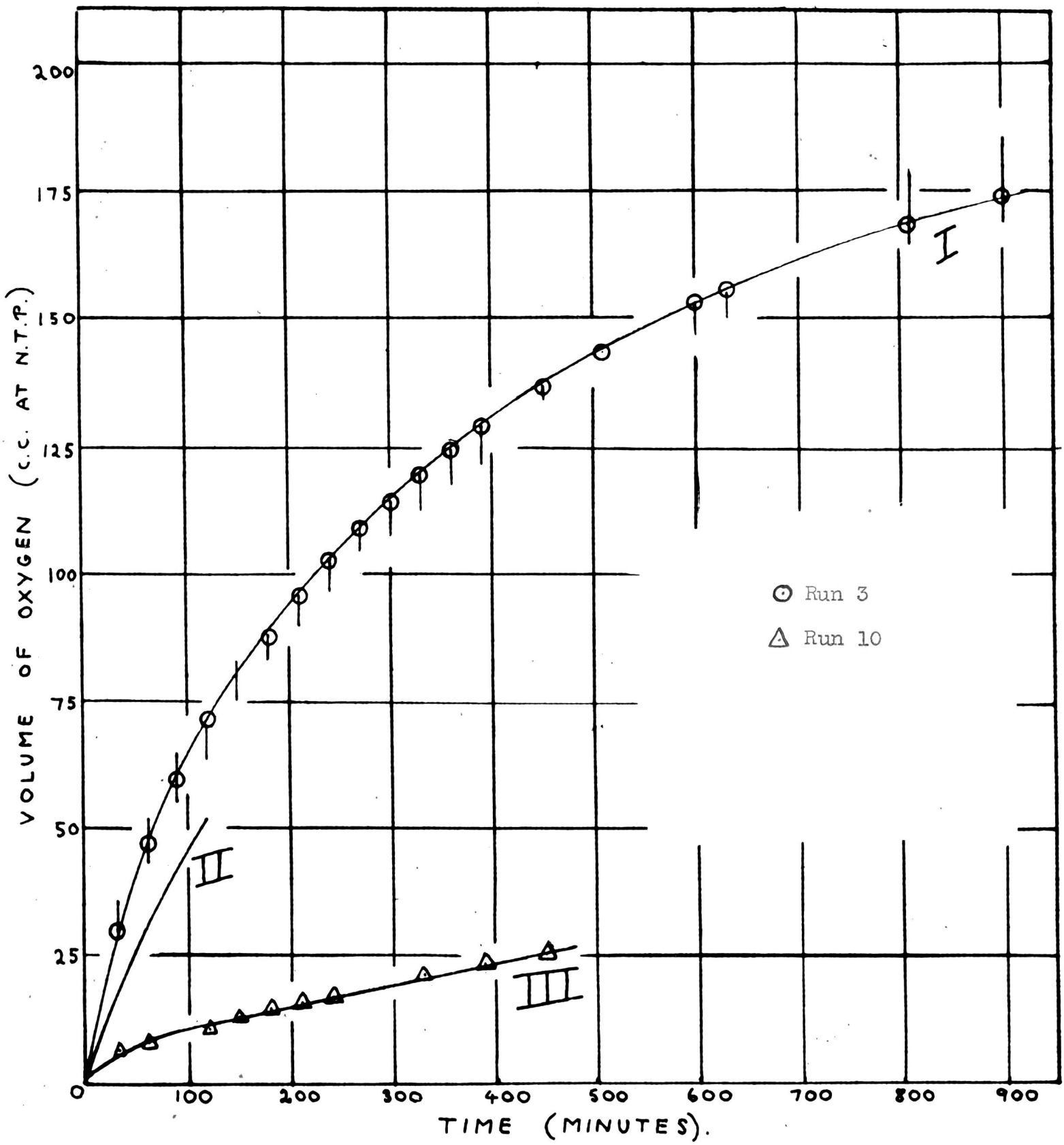
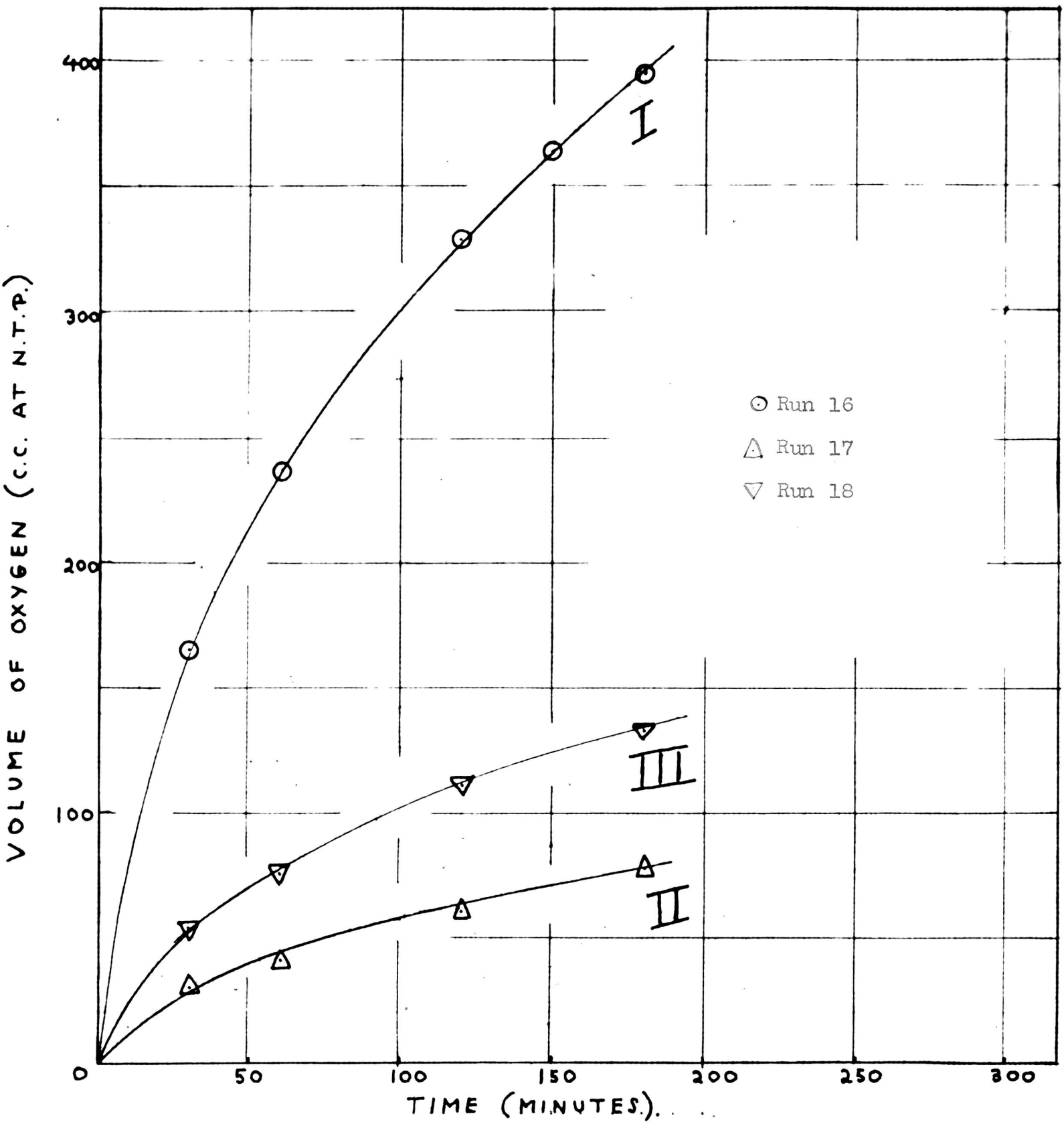

200
175
150
125
100
75
50
25
0
VOLUME OF OXYGEN (C.C. AT N.T.P.)
100
200
300
400
500
600
700
800
900
TIME (MINUTES).
I
II
III
Run 3
Run 10

Fig.22


VOLUME OF OXYGEN (C.C. AT N.T.P.)
400
300
200
100
0
50
100
150
200
250
300
TIME (MINUTES).
I
II
III
Run 16
Run 17
Run 18

were shaken and in runs 8 and 9 the suspension was stirred by means of a stirrer passing through a mercury seal (the method adopted by King). No significant variation in the volume of oxygen evolved after 300 minutes could be detected (Table 6, page 52).

Comparison of Curve I of Fig.20 with Curve I of Fig.21 shows that the general shape of the decomposition curve was the same for H-type and U-type charcoals. It will be seen that the amount of oxygen evolved in any given time in the case of runs 14 and 15 (H-charcoal) is about twice that for runs 1 to 9 (U-charcoal). The H-charcoal possessed a much larger specific surface area than the L-charcoal, and was treated with more concentrated hydrogen peroxide (ca. 18 volumes, as against ca. 10 volumes). These factors would account for the higher rate.

The results of experiments in which 25 ml. of specially prepared hydrogen peroxide of 11 volumes strength were shaken without charcoal present (runs 12 and 13), indicated that no appreciable decomposition of the peroxide by the glass surface of the reaction vessel occurred. With H-charcoal present (runs 17 and 18), the specially prepared peroxide gave curves (Fig.22, Curves II and III respectively), similar in shape to those obtained

with the other peroxide preparations.

Curve II of Fig.21 is the decomposition curve (at 25°) obtained by Larsen and Walton[25]. These workers used sugar charcoal (activated in a manner which made it comparable with an H-charcoal), and hydrogen peroxide solutions free from inhibitor. In agreement with the results of the present work, there is no evidence of β -activity. It does not seem to be possible to offer any explanation of King's results for H-charcoals. Although in the present work, all relevant factors (viz. source of peroxide and method of agitation) in the experimental conditions have been varied, his decomposition curve could not be reproduced.

Curve III of Fig.21 is the plot of the results of run 10, in which an L-charcoal was treated with inhibitor-free hydrogen peroxide at a concentration similar to that used in the experiments corresponding to Curve I. It is evident that activation of the charcoal at 400° has caused a pronounced decrease in the activity of the charcoal, since only 25 ml. of oxygen have been evolved in 450 minutes compared with ca. 138 ml. when an unactivated charcoal was used (Curve I). This is in qualitative agreement with results of King, who reported that the volumes of oxygen evolved during 180 minutes by the action of H- and L-charcoals were 62 ml. and 9 ml. respectively.

Schilov, Schatunovskaja and Tschmutov[26] found that a charcoal which had been treated with hydrogen peroxide could sorb base. This, together with the claim made by King that an H-charcoal developed other L-charcoal characteristics (viz., β-activity, and low p_H of aqueous suspension) after being in contact with hydrogen peroxide for about 2 hours, suggested that the full L-character (viz., high oxygen-content and high base-sorbing capacity) might be developed after 2 hours. Accordingly, the base-sorption of all the hydrogen peroxide treated charcoals was determined, and the data are recorded in the last column of Table 7 (page 54). Δ NaOH denotes the difference between the sorption observed after treatment with hydrogen peroxide, and the small amount of sorption obtained with the untreated charcoal. It is evident from the data for U-charcoals, that no marked increase in base-sorption capacity is developed when such charcoals are treated with hydrogen peroxide. In view of this result, there appeared to be no justification for departing from the conventional gas-activation method when preparing L-type charcoal from un-activated material. However, the data proved to be of value in another direction, as will now be shown.

While it is true that there is no sudden fall in the rate of evolution of oxygen to a constant

low value (i.e., β -activity), there is no doubt that the rate decreases with time. At low concentrations this could arise, at least in part, from decrease in the concentration of peroxide as the result of decomposition. However, at the highest concentration used in the present work, this effect would be very small. In run 16 (Curve I of Fig.22), the initial amount of peroxide contained 2440 c.c. of available oxygen. Of this, only about 400 c.c. had been evolved in 180 minutes, although by then the rate of evolution had fallen very appreciably. It must therefore be concluded that the activity of the carbon surface, as regards the production of gaseous oxygen, decays as the reaction proceeds. Larsen and Walton (loc.cit.) arrived at the same conclusion, since in experiments designed to test the matter, it was found that the rate decreased from 2.09 to 0.22 ml. per minute, while the peroxide concentration changed by only 5 per cent. These workers observed also that if a charcoal already treated with peroxide was immersed in a fresh solution of the original concentration, the rate, after a slight increase, reversed to the value previously attained. This was confirmed in the course of the present work, and supports the view that the charcoal becomes inactivated in some way.

Now the increased capacity for sorbing base

presumably means that the charcoal reacts with the peroxide in such a manner that a layer of chemisorbed oxygen is formed upon the surface of the charcoal. It seems reasonable to suppose therefore, that the decomposition of the peroxide to give oxygen, is initiated on the bare carbon surface of the H-charcoal, and that the decay in activity is due to the covering of the surface with chemisorbed oxygen. King postulated that by interaction with peroxide, the "basic oxide" of an H-charcoal, supposed to be catalytically active, was converted into the inactive "acidic oxide". In the light of the evidence in favour of Steenberg's explanation of the sorption of acids by H-charcoal (see page 7), the present interpretation of the decay appears preferable to that of King.

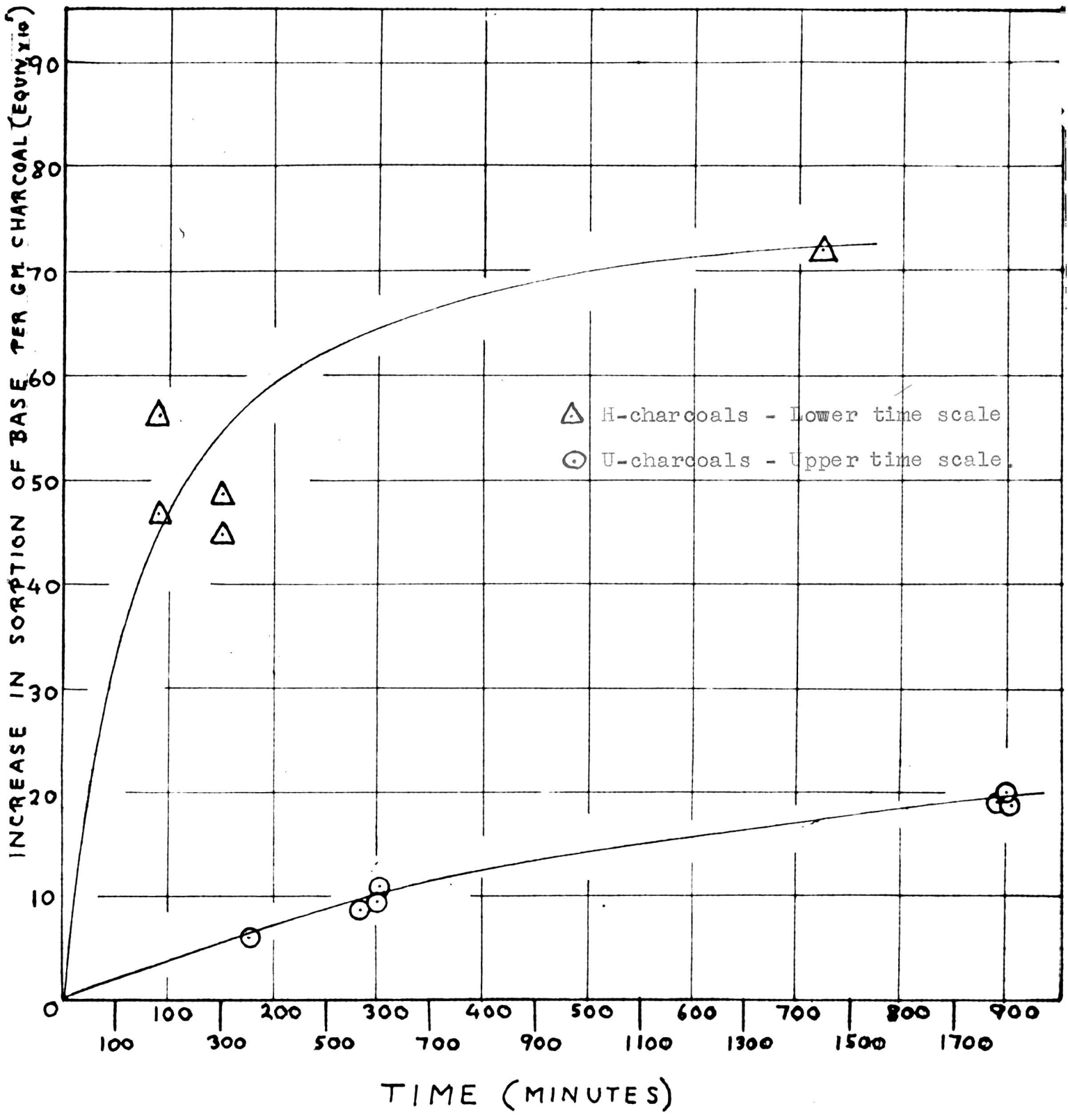
The view that the cause of the inactivation of the charcoal surface is the formation of the oxygen layer responsible for the sorption of base is consistent with the manner in which Δ NaOH varies with the period of contact between charcoal and peroxide solution. Table 7 (page 54) shows that in the case of the most concentrated peroxide, Δ NaOH was 56.3×10^{-5} equivalents for 3 hours (run 16), and 72.2×10^{-5} equivalents for 24 hours contact. Thus the rate of increase of Δ NaOH fell off markedly in the neighbourhood of 3 hours,

possibly before this. From Curve I of Fig.22 it appears that the rate of evolution of oxygen in run 16 continuously decreased during the first 2½ hours and then became approximately constant. Up to 2-3 hours the inactivation was relatively rapid, because the oxidation of the charcoal surface was proceeding vigorously. Beyond this point the formation of the oxygen layer, and therefore the inactivation, took place so slowly that the rate of evolution of gas was approximately constant.

In Fig.23 all the values of $\triangle$ NaOH obtained with H-type charcoal (Table 7) are plotted against period of contact (lower time scale). They may be said to lie approximately on a common curve (the upper curve in Fig.23), despite wide variation in the concentration of peroxide (17.5 to 97.2 volumes). This independence of concentration may be reasonably explained on the assumptions that the oxidation of the charcoal surface is due to the action of adsorbed peroxide, and that, at the concentrations in question, the adsorption was maintained at its maximum value throughout the period of contact. Thus, the oxidation would always proceed at the same effective concentration of peroxide, while the bulk concentration varied with the experiment and during any one experiment.

Although the rate of oxidation of the charcoal surface is independent of peroxide concentration

Fig. 23.


INCREASE IN SORPTION OF BASE PER GM. CHARCOAL (EQUIV. X10⁻⁴)
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
100
300
500
700
900
1100
1300
1500
1700
TIME (MINUTES)
H-charcoals - Lower time scale
U-charcoals - Upper time scale.

(at specially high concentrations), this is not the case for the production of oxygen gas. The data for runs 14, 15 and 16 (all H-charcoals), which gave similar values for $\triangle$ NaOH, indicate that a five-fold increase in concentration more than doubled the volume of oxygen produced in 180 minutes. This result suggests that the decomposition of the peroxide to give oxygen is a chain reaction, initiated on the bare carbon surface, and propagated in the bulk of the solution. In view of the metallic behaviour of carbon under certain conditions, it is not unreasonable to suppose that the mechanism is similar to that proposed by Weiss[27] for the catalytic decomposition of hydrogen peroxide by metals. According to this mechanism, the following reactions would be involved:

(1) $C + H_2O_2 \longrightarrow C^+ + OH^- + OH$

(2) $OH + H_2O_2 \longrightarrow H_2O + HO_2$

(3) $HO_2 \rightleftharpoons H^+ + O_2^-$

(4) $O_2^- + H_2O_2 \longrightarrow OH^- + OH + O_2$

(5) $H_2O_2 \rightleftharpoons H^+ + HO_2^-$

(6) $C^+ + HO_2^- \longrightarrow C + HO_2$

(7) Chain-breaking reactions.

On the basis of this scheme, it appears conceivable that fixation of oxygen by the charcoal surface might occur as the result of the reactions

$$2C^{+} + O_2^{-} \longrightarrow \begin{matrix} C & - & O \\ | & & | \\ C & - & O \end{matrix}$$

or

$$C^{+} + O_2^{-} \longrightarrow C\begin{matrix} O \\ | \\ O \end{matrix}$$

However, these suggestions are to be regarded as merely tentative, and further experiments, specially designed for the purpose, would be required to elucidate the mechanism of the production of oxygen and that of the oxidation of the carbon surface.

The lower curve in Fig.23 (upper time scale) illustrates the manner in which $\triangle$ NaOH varied with time of contact in the case of U-charcoals. That the magnitude of $\triangle$ NaOH was less than in the case of the H-type charcoals is to be expected, since the specific surface area would be less. Moreover, the concentration of peroxide was relatively low (about 10 volumes), and it is therefore possible that the adsorption of peroxide was below the saturation value. This would also account for the falling off in the rate of increase of $\triangle$ NaOH when the period of contact was prolonged. It will be seen that there is no sudden decrease in the rate, similar to that observed with H-type charcoals.

It may be that the activation creates a number of sites on the carbon surface, markedly susceptible to oxidation. These would be readily attacked, giving the initial rapid rise in Δ NaOH, and thereafter the oxidation would proceed on a surface comparable with that of an unactivated charcoal, and therefore at a corresponding low rate.

In the last place, it should be mentioned that the charcoal which gave the highest value of Δ NaOH (72.2×10^{-5} equivalents) was treated with potassium chloride solution and the system examined for liberated acid in the usual way. No liberation of acid was observed, apart from a small amount which might well have been obtained if water, instead of salt solution, had been employed (cf. page 117). This result indicated the entire absence of acidic hydroxyl groups.

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SUMMARY

1. The chemical behaviour of oxygen chemisorbed on charcoal activated at 400° (L-type charcoal) has been investigated, with the primary object of elucidating the mechanism of the sorption of base from aqueous solution.

2. A study has been made of the interaction of L-type charcoal with aqueous solutions of neutral salt, in particular with respect to the influence of (a) the concentration of the salt, (b) the ratio : weight of charcoal/volume of solution, and (c) pretreatment of the charcoal with strong inorganic base and acid, upon the amount of liberated hydrogen ion.

The results indicate (a) that on the assumption that the liberation of acid is due to ionic exchange involving ionisable hydroxyl groups (phenolic or carboxylic), then only a very small proportion of the oxygen is present in the form of these groups, and (b) that none of the oxygen is present as acid anhydride groups.

3. The interaction of L-type charcoal with aqueous solutions of sodium arsenite, in presence and in absence of gaseous oxygen, has been examined.

It has been shown (a) that the chemisorbed oxygen is capable of direct oxidation of arsenite to arsenate, (b) that L-type charcoal does not catalyse the oxidation of arsenite by gaseous oxygen, and (c) that arsenite and/or arsenate are strongly sorbed by the oxygen layer.

4. An investigation has been made of the behaviour of charcoal when heated with Grignard reagent (methyl magnesium iodide in di-isoamyl ether) at 181°, particularly in regard to the influence of the type of charcoal (L or H) upon the nature and rate of formation of gaseous products.

It was found that, under the given conditions, (a) there was an evolution of gas proceeding at a constant rate, the same for both L- and H-charcoal, and continuing throughout the maximum period of observation (7 hours), (b) an additional evolution of gas occurred proceeding at a higher rate and terminating under 7 hours. In this case the amount of gas was very much greater with L- than with H-charcoal. (c) According to analysis, the only gaseous products were methane and ethane. It was also found that (d) there was little evidence of reaction to give gaseous products when the ether was heated with or without charcoal, and (e) gaseous products were formed in considerable

amount when the Grignard reagent was heated alone.

On the basis of these results it is concluded that (i) the methane was produced by some action of the chemisorbed oxygen present on the charcoal, (ii) the ethane probably arose from thermal decomposition of the Grignard reagent.

5. The effect of treatment of L-charcoal with Grignard reagent or di-isoamyl ether upon the sorption of base has been examined. It appears that the capacity of the charcoal to sorb base was reduced by treatment with the reagent to a minimum value which was reached in the period of time necessary for the complete evolution of methane. Treatment with the ether influenced the sorption in exactly the same way.

As a working hypothesis, it is suggested that (a) the decrease in sorptive capacity was due to loss of chemisorbed oxygen, by reaction with the ether to give hydroperoxide and (b) that the methane was formed by interaction between the hydroperoxide and the Grignard reagent. It has been shown that these assumptions lead to values for the ratio : Gm. Atoms of chemisorbed oxygen/Moles of sorbed base, which are very similar to those obtained by other workers by direct determination. If the hypothesis is correct, the sorption cannot be due

to hydroxyl and lactone groups on the charcoal surface.

6. The sorption of base in the presence of alcohol has been examined. No increase in the sorption, as reported by some workers, was observed, the alcohol being without effect, in keeping with the observations of Steenberg.

7. In view of the lack of evidence for a chemical interpretation of the sorption of bases, it is suggested that attention should be directed to the possibility, that the base may be physically adsorbed.

8. The decomposition (at 20°) of aqueous solutions of hydrogen peroxide in the presence of charcoal has been studied with respect to the influence of (a) type of charcoal, (b) source of peroxide, and (c) method of agitation, upon the rate of evolution of oxygen. The results agree with those of Larsen and Walton in showing a gradual decay in the rate, instead of the sudden change reported by King.

It has been shown that the treatment with hydrogen peroxide increases the sorptive capacity of the charcoal for base, indicating that the charcoal surface becomes covered with chemisorbed

oxygen. The decay in the rate of evolution of oxygen is therefore ascribed to inactivation of the carbon surface by the formation of the oxygen layer.

The relatively small increase in sorptive capacity which resulted from prolonged treatment with very concentrated peroxide, showed that, as a means of producing L-charcoal, the procedure was inefficient compared with the normal method. It was observed that in the case of H-charcoals the rate of increase of sorption was initially rapid but soon fell to a much lower value. The effect is attributed to the existence of sites on the carbon surface, with different degrees of activity.

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